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INKS:

THEIR COMPOSITION AND MANUFACTURE.

To make good inke

Take a quart of rayne water, or clarett
wyne, or read vinegar not beinge to sharpe
5: ounces of galls / 4: ounces of copperas /
3: ounces of gumm / beat the galls and
copperas a little then put :2: [illegible] of the water
& lett them stand ~~as before~~ stroke the
~~gum~~ as sone be putt in the fire /
after :5: dayes standinge boyle them a
little but verye little ~~&~~ the [illegible]
yf ye will have it shine putt in a peny=
worth of white suger

INKS:

THEIR COMPOSITION AND MANUFACTURE.

INCLUDING METHODS OF EXAMINATION AND A FULL LIST OF ENGLISH PATENTS.

BY

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Editor of *The Analyst*, Cantor Lecturer on Inks.

AND

T. C. HEPWORTH.

With 69 Illustrations, including 4 Plates.

THIRD EDITION. THOROUGHLY REVISED. RE-SET.

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PREFACE TO THE THIRD EDITION.

The exhaustion of the Second Edition of this work has afforded the opportunity of thorough revision throughout, and every section has been carefully examined and brought in line with present knowledge. Sales of the book were retarded during the war, and when the call for this edition came I was engaged upon the manuscript of a companion book, *Documents and their Scientific Examination*, and revision was delayed. The section in the present work relating to the detection of forgery has been brought up to date, but reference may be made to the other book for much fuller treatment in its many details of this wide and complicated subject. The classified list of Patents has also been brought up to date.

In this edition (as in the Second) I have differentiated the chemical work, for which from the first I have been solely responsible, by the use of the term "the writer," as in the first edition my old friend, T. C. Hepworth, a scientific photographer, collaborated with me in the preparation of the manuscript.

In addition to those whose assistance we acknowledged in the First Edition, it gives me pleasure also to thank those who have helped me with this edition.

Among them I would especially mention Mr. *Albert Osborn*, of New York, who has again allowed me to quote results and reproduce illustrations from his standard work, *Questioned Documents*; Mr. *A. Lucas*, of the Government Laboratory, Cairo, to whom I am indebted for details

of his experiments on the carbon inks of Egypt and for various specimens; and Dr. *M. Nierenstein*, who has given me much information on galls and tannins, and who has also been good enough to read and criticise the proof sheets of the section of the book dealing with that subject.

My best thanks are also due to Messrs. *Torrance & Co.* for information as to their latest types of machinery for printing inks, and for the loan of blocks, and to Messrs. *B. Winstone & Sons*, who have kindly given me a description of the preparation and properties of rotagravure inks, and an illustration of the grinding mills used by them for their manufacture.

C. A. M.

WHITE COTTAGE,
THE COMMON,
AMERSHAM.
May, 1924.

PREFACE.

Some three years ago we were engaged in a scientific inquiry as to the composition of certain fluids used as writing ink. As this work led us beyond the limits anticipated, and to the making of many experiments not actually required at the time, and as there is need for a volume dealing adequately with the subject, we thought it advisable to embody the results in book form. We found, it is true, a few small books on ink and many allusions to ink-making in old volumes and isolated papers in scientific journals; but it seemed to us that the matter required more comprehensive treatment, and the present work may be regarded as an attempt to supply that want.

As far as time permitted we have tested the various formulæ quoted, but, as may be seen by reference to the patent list at the end of the book, there are so many cases of slight variations in composition that we have often contented ourselves with a record of the statements put forward.

We have pleasure in tendering our best thanks to those who have assisted us in our work.

To Mr. *R. M. Prideaux*, in particular, we are indebted for the excellent drawings of the various galls (pp. 39 to 51), the details of which could not have been nearly so well shown by photography.

Messrs. *Newman & Co.*, of Soho Square, were good enough to afford us much information with regard to sepia preparations, and to supply us with dried specimens, etc., for analysis.

The photographs of fossil cephalopoda were taken by us at the Geological Museum, Jermyn Street, by the courtesy of the Curator.

To the authorities at Kew we are indebted for permission to photograph in the Museum and in the Herbarium.

The *Badische Company* kindly supplied us with specimens of aniline dye-stuffs and much valuable information regarding them.

We have also to thank *Messrs. Keller & Co.*, who have kindly allowed us to use certain blocks illustrative of printing-ink machinery, and have sent us samples of various permanent colours.

Lastly, our thanks are due to *Messrs. Madderton & Co.*, of Loughton, for specimens of permanent preparations made by them.

C. A. M.
T. C. H.

Gray's Inn, London, W.C.,
August, 1904.

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HISTORICAL INTRODUCTION.

ANCIENT EGYPT.—The earliest use of a liquid which can be described as "ink" is found in those documents on papyrus which have been among the archæological treasures of Egypt. Although the history of Egypt has been traced back for a period of more than four thousand years, and papyrus was employed as a writing material there from very remote times, the oldest specimen of the material extant is a roll which dates from B.C. 2500.* This possibly refers to the oldest specimen which bears decipherable characters, for Professor *Flinders Petrie* has found fragments of papyri which date from a thousand years earlier.† As Egypt is still the subject of exploration, and as perishable articles have been found of a still earlier period than that last mentioned, we may reasonably hope that ink-written records may some day come to light which will carry back the history of the country to a more remote time. Professor *Flinders Petrie* found in one tomb, dating from 3500 B.C., baskets, a coil of palm rope, wooden mallets, and chisels left behind by the workmen, together with some pieces of papyrus which were almost white; and he attributed the excellent condition of these things to the preservative nature of the clean dry sand in which they had been buried for so many centuries.‡

It seems probable that carbon ink was prepared in solid sticks as in China, although, judging by the fact that reed pens (see Fig. 1) were used on some of the papyri about the 7th century B.C., the ink must also have been used in a more fluid form. This is confirmed by the discovery of ink-stands still containing some of the dried ink (see Fig. 2). Mr. *A. Lucas* has given an account of the composition of the remains of ink from an ink-stand of the 16th century B.C., and has shown that the basis of this is carbon.§ In fact, all the ancient Egyptian inks appear to have been essentially

* *British Museum Guide*, 1896, p. 312.
† *Journal of the Camera Club*, Nov. 1897.
‡ *Ibid.*
§ *Analyst*, 1922, xlvii., 9.

carbonaceous in character, for such ink is present on potsherds (Fig. 4) and on papyri as late as the 5th century B.C.

OLD PAPYRI.—In Case A (Greek Papyri), British Museum, can be seen a number of specimens dating from the first century of the Christian era, and although in many cases the papyrus is merely in fragments, the ink is as black as it was the day it was applied. The lettering in many of these papyri is extremely beautiful, and compares very favourably with much of the handwriting that some of us have to decipher to-day. And it would seem quite clear from an examination of many of these writings that the implement employed was a pen and not a brush. The papyrus in some instances is of a very light drab colour, and on this surface the old writing stands out with startling distinctness; but when the material has assumed a dark brown or yellow tint, the writing is not so distinct, although the quality of the ink is often quite as good.

That papyrus was not a cheap material is shown by a specimen here, labelled "Aristotle on the Constitution of Athens. The only extant MS. of the work, brought from Egypt in 1890. Written about A.D. 100, in four rolls, in four different hands, on the back of the papyrus which had already been used (in A.D. 78-79) for the accompts of a farm-bailiff named Didymus, near Hermopolis."

Another specimen of great interest lies close to the one first mentioned—namely, fragments of the *Theogonia* of Hesiod. It is written in a firm and large handwriting in very black ink, and the label tells us that its date is probably the fourth or fifth century, "contemporary with the early MSS. on vellum, and so marking the transition from the one material to the other."

PROGRESS OF WRITING.—The various specimens shown in the King's Library at the British Museum, in Cases A—E, are designed to illustrate the progress of writing from the second century B.C. to the fifteenth century of our era, and at the same time they give some idea of the kind of ink employed during the period covered. The basis of the black ink used on papyrus by the ancient scribes was undoubtedly carbon, a substance which had the advantage of being easily procurable, while at the same time it was indestructible except by fire. It was probably prepared, not only in the form of lamp-black, but also in some cases in the form of vegetable or animal charcoal, and was mixed with gum, oil, or varnish. Possibly, for the finer writing, water, with gum or glue as a binding material, was the medium mostly employed, for it would flow more readily from the reed pen or quill used by the writer.

It is certain that the art of writing has a remote antiquity, and that the power of recording thoughts in this way marks a distinct

line of demarcation between civilised man and the savage. It is a matter of interest to consider the many different materials which have been used for writing upon in early times besides papyrus. Soft wood cut into slices and planed and polished was used in various countries, the pen being a metal stylus, which simply scratched or indented the material. Later on, the wood tablet with a thin coating of wax was employed, and the writing upon it in the case of ephemeral memoranda could be quickly effaced. Bark and palm leaves were also used for writings of a temporary character, and in some countries in later times both linen and silk have been so employed. The Chinese are credited with the invention of paper anterior to the Christian era, a statement which need not excite surprise when we remember that they anticipated Europe in the invention of printing by nearly a thousand years. We may assume that for many centuries before this the art of writing in China had been brought to some degree of perfection.

Among the Roman antiquities found in Britain, which are now deposited at the British Museum, are many specimens of the stylus in ivory, bronze, etc., and some of these are armed with a sharp projection, with which guiding lines could be ruled across the waxen surface of the tablets. The reed pen was commonly used for writing on papyrus, and the steel pen was foreshadowed by a few specimens in bronze found in Italy, and one in England. This last is among the Romano-British antiquities in the British Museum. It consists of a tubular piece of bronze, about five inches in length, which has at one end a split nib, while the tube is gradually reduced in size towards the other extremity, where it ends in a solid piece, which was probably used for pressing down the wax in order to efface the writing.

In the Mediæval Room at the British Museum may be found many very rare specimens of writing tablets, some belonging to a period before the seventh century. Some of these are what is known as "consular diptychs," so-called because these folded tablets were at one time sent as ceremonial presents, by the Roman consuls on their appointment, to official persons or to friends. Many of these tablets are of ivory and are beautifully carved, and the slabs or plaques are sometimes of such a size that the tusks procurable at the time they were made must have been of unusual dimensions, or the workmen had some means of bending the material, the secret of which is now lost.

HERCULANEUM FRAGMENTS.—In 1821 Sir *Humphry Davy* read a paper before the Royal Institution,* in which he described

* *Trans. Roy. Soc.*, 1821, ii., 191.

a number of experiments that he made with some fragments of papyri which had been found in the ruins of Herculaneum. Of some of these papyri he says: "The black ones, which easily unroll, probably remained in a moist state without any percolation of water; and the dense ones, containing earthy matter, had probably been acted upon by warm water, which not only carried in to the folds earthy matter suspended in it, but likewise dissolved the starch and gluten used in preparing the papyrus and glue of the ink, and distributed them through the substance of the MSS."

He made further experiments in the Museum at Naples. And of some of the MSS. he says: "These MSS. had been so penetrated by water that there were only a few folds which contained words, and the letters were generally erased, and the charcoal which had composed them was deposited in the folds of the MSS."

He makes some general observations, of which the following are worth noting:—

"I looked in vain amongst the MSS. and on the animal charcoal surrounding them for vestiges of letters in oxide of iron; and it would seem from these circumstances, as well as from the omission of any mention of such a substance by *Pliny*, that the Romans, up to his period, never used the *ink of galls and iron* for writing: and it is very probable that the adoption of this ink, and the use of parchment, took place at the same time. For the ink, composed of charcoal and solution of glue, can scarcely be made to adhere to skin; whereas the free acid of the chemical ink partly dissolves the gelatine of the MSS., and the whole substance adheres as a mordant; and in some old parchments, the ink of which must have contained much free acid, the letters have, as it were, eaten through the skin, the effect being always most violent on the side of the parchment containing no animal oil." *

The disintegration of the papyrus by the action of water, alluded to by Sir *Humphry Davy*,† will be readily understood when we remember that this ancient writing material was made of thin strips cut from the reed and cemented together. The strips were laid side by side, and then other strips were laid across them at right angles, the whole being stuck together and placed under pressure so as to form a paper-like sheet. Papyrus was first used as a single sheet, or in lengthy documents as a long roll of different

* *Trans. Roy. Soc.*, 1821, ii., 191.

† Several illustrations are attached to Sir H. Davy's paper, mostly showing fragments of papyrus with writing upon them. Fig. 1 shows an ink-pot, a reed pen, and a roll of papyrus, and Fig. 2 a box containing rolls of papyrus.

sheets joined together. Later on papyrus leaves were bound together as in a book. At a very early period papyrus was imported into Greece and Italy. It continued to be the chief writing material in Egypt until the tenth century, and was largely used in Europe after vellum had been introduced.

CARBON INKS.—We give illustrations (Figs. 1, 2, and 3) of various

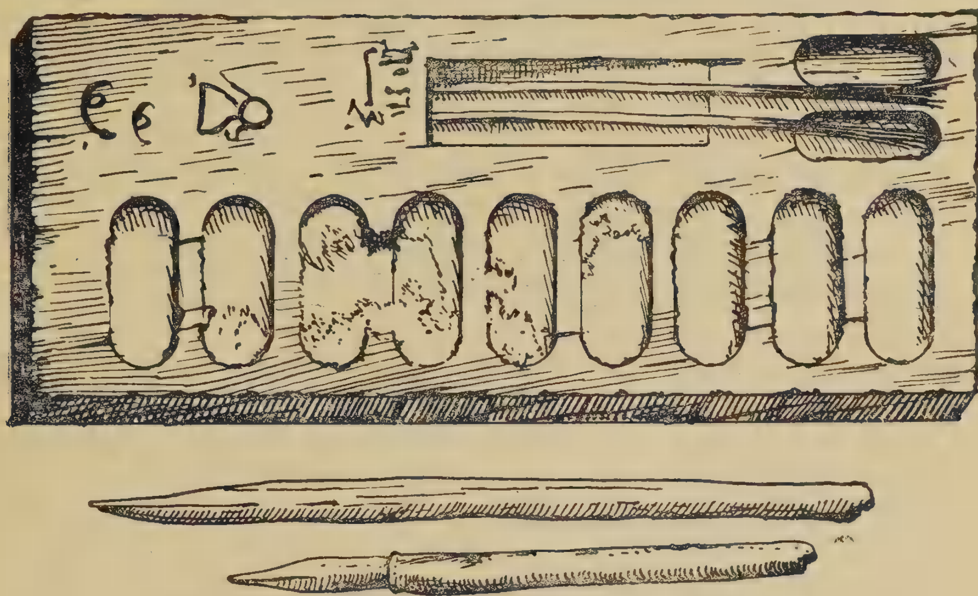


FIG. 1.—Egyptian Palette, Brushes, and Pens.

writing implements, dating back to about 1500 B.C., which are exhibited in the Egyptian department of the British Museum. The titles of these pictures sufficiently explain their nature.

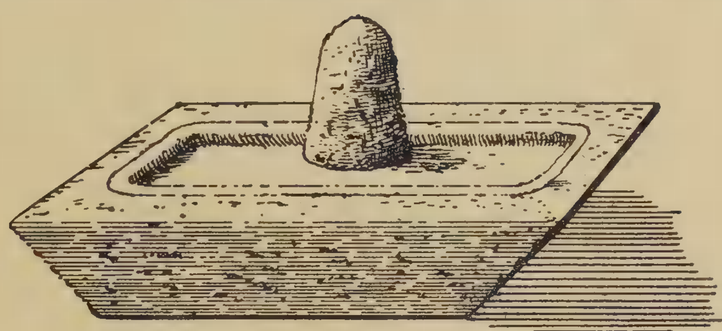


FIG. 2.—Egyptian Slab and Muller.

Fig. 4 represents a typical fragment of a potsherd, for which the writer is indebted to Mr. A. Lucas.

Chinese, or Indian ink, as it is commonly called in this country, was made at a very early period, according to Chinese historians

as far back as between B.C. 2697 and 2597, the inventor being one *Tien-Tcheu.* Full particulars of the way it is manufactured are

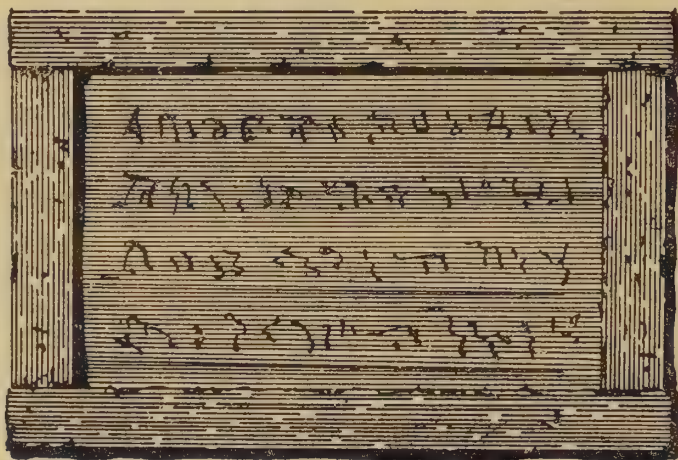


FIG. 3.—Egyptian Wax Tablet.

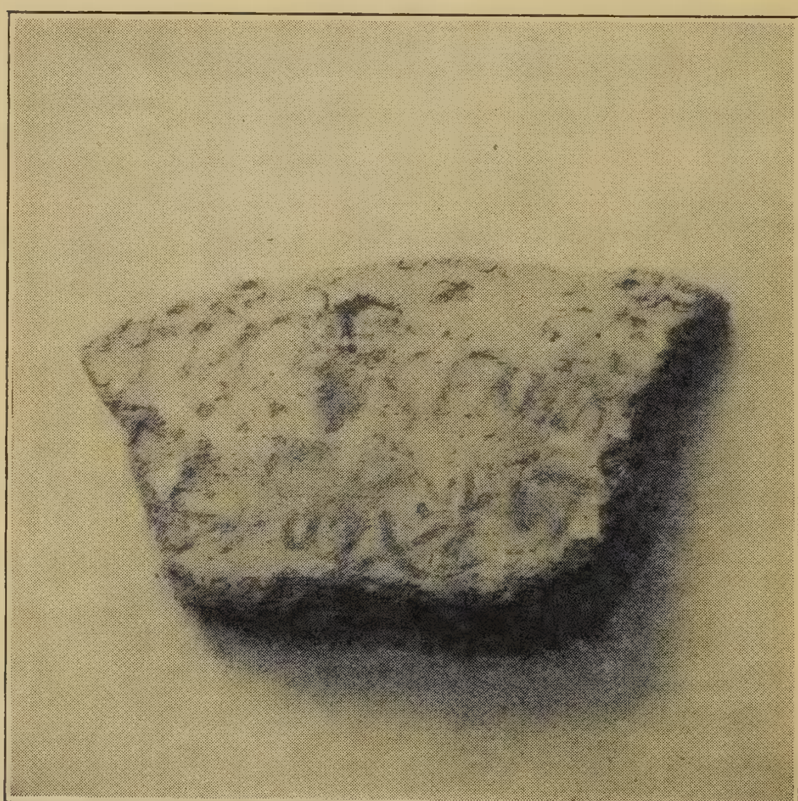


FIG. 4.—Ancient Egyptian Potsherd, with writing in Carbon Ink.

given in a subsequent chapter. Its base, like that of early Egyptian and other inks, is carbon.

Dioscorides,* physician to Antony and Cleopatra (B.C. 40-30), in a dissertation on the medicinal use of herbs, gives the proportion of lamp-black and oil to be used in the manufacture of ink (*atramentum*).

Vitruvius,† the Roman engineer and architect (B.C. 30-A.D. 14), describes a method of preparing ink for mural decoration : soot from pitch-pine being collected from the walls of a specially constructed chamber, mixed with gum (*glutinum*), and dried in the sun.

Pliny ‡ (A.D. 23-79) mentions that writing can be readily sponged out, and also speaks of the different varieties of ink in use in his time.§

Martial || (A.D. 100) sends a sponge with his newly written book of poems, so that the writing could be effaced if the composition did not merit approval.

It is clear from these last two references that an oil and carbon ink cannot be meant, for it could not have been removed by means of water. Either a preparation of lamp-black and gum must be referred to, or possibly an ink made from sepia. *Persius* ¶ (A.D. 34-62) refers to ink becoming too thick and too pale on adding water, and uses the word "sepia." *Cicero*, a century earlier, also refers to the use of this natural ink.

Many other natural inks, but of vegetable origin, have been used for writing and marking in various parts of the world. All are fully described in a later chapter.

IRON GALL INKS.—The monk *Theophilus*,** who wrote an encyclopædia of Christian art in the eleventh century, described, among other things, a method of preparing writing ink from thorn wood. An aqueous extract of the wood was evaporated to dryness and the powder mixed with green vitriol. This is the earliest reference which we have been able to find to an iron-tannin ink.

Albertus Magnus (A.D. 1193-1280) also refers to the preparation of an ink from green vitriol in his treatise *De Rebus Metallicis*.

A treatise was published in Paris in 1393, under the title of *Menagier de Paris*, in which a method of preparing an iron ink from galls was described.

The *Liber Illuminastarum* (A.D. 1500) gives the following directions for the preparation of writing ink :—

Integra sit galle, media sit uncia gummi
Vitriola quarta. Apponas octo falerni.

---

* Folio edition, 1598, in Greek and Latin.

† *De Architectura*, lib. vii., 10.

‡ *Nat. Hist.*, xxvii., § 52.

§ *Ibid.*, xxxv., § 41.

|| iv., 10.

¶ *Satires*, iii., 13.

** Theophilus, *Diversarum Artium Schedula*, lib. i., chap. xl., p. 48, Hendrie's translation.

Wecker, a doctor of medicine of Basle, in 1612 * described the preparation of an indelible ink compounded of lamp-black and linseed oil. He also alludes to coloured inks, and in particular to sympathetic inks.

Peter Canneparius, professor of medicine at Venice, wrote on inks, *De Atramentis*, etc.,† and described the composition of various sorts of ink. Black ink is referred to as being made from galls and vitriol, and coloured inks are procured from gums, woods, the juices of plants, etc.

Incidentally he quotes a popular Italian proverb :—

Una due tre e trenta
A far la bona tenta.

That is to say, one part of gum, two of vitriol, and three of galls in thirty parts of water.

Sir *E. Maunde Thompson* remarks ‡ that ink differs in tint at various periods and in different countries, and that whilst in early MSS. it is pure black, or slightly brown, in the Middle Ages it varies a good deal according to age and locality. He also tells us that in Italy and Southern Europe the ink of MSS. is generally blacker than in the north, and that a Spanish MS. of the fourteenth or fifteenth century may usually be recognised by the peculiar blackness of the ink. The ink of the fifteenth century is often of a faded grey colour.

THE LINDISFARNE GOSPELS.—The MS. known as *The Lindisfarne Gospels*, or *The Gospels of St. Cuthbert*, or *The Durham Book*, is of great interest, for it is one of the earliest, and certainly one of the most beautiful, MSS. on vellum in the British Museum. Four paintings representing the Evangelists precede the respective Gospels, and three of them are shown in the act of writing. It is noteworthy that the pen, very plainly shown in the figure of St. Mark, is cut like a quill. This MS. is unusually fresh and clean, although according to tradition it was, upon one occasion, lost at sea in a violent storm, and was recovered at low tide by the intervention of St. Cuthbert. The date at which it was written is supposed to be at the close of the seventh century. This valuable MS. is placed in a case next to an MS. of Shakespeare's time ; and although one is nearly nine centuries older than the other, the ink of the earlier work is perfectly black and well preserved, whilst that of the other is very much faded.

* *De Secretis*, lib. xvii., 713.

† London edition, 1660.

‡ *Greek and Latin Palæography*.

With regard to the later MSS. on paper and parchment, and confining our attention to those which are exhibited in the open cases at the British Museum, there is little to complain of in the quality of the ink. The writing is mostly of a rich dark-brown, and we may take it that if an MS. has thus preserved its freshness for three or four centuries the ink may be regarded as permanent enough for all practical purposes. It is interesting to note that in some of these MSS. two different inks have been used on the same page. For instance, we have here the Bible which belonged to Milton, on the first page of which he has entered in his own hand memoranda of the births of himself and members of his family. All the entries are written in a dark ink, with one exception—this is the entry referring to the birth of his daughter Deborah on "the 2nd of May, being Sunday, somewhat before 3 of the clock in the morning, 1652." The ink in this case is very pale, the loss of colour being possibly due to dilution.

TRANSITION FROM CARBON TO GALL INKS.—The transition from carbon ink to that made from galls and iron is a very gradual one, and we find many writers deploring the effects of that change. Mr. *Astle* * (1803) complains that the modern ink is not comparable with that used by the ancients, and attributes the deterioration to negligence in manufacture. He writes: "Gall-nuts, copperas, and gum make up the composition of our inks, whereas soot or ivory black was the chief ingredient in that of the ancients."

Another paragraph from the same source is worthy of quotation:—

"Although paper is now chiefly made from linen rags beaten to a pulp in water, yet it may also be made of nettles, hay, straw, parsnips, turnips, colewort leaves, flax, or of any fibrous vegetable."

This extract, written more than a century ago, is interesting in view of the circumstance that linen rags are now only used for the very finest grades of paper. Wood pulp is now largely employed, and there is ground for the fear that in the future it will not be the quality of the ink which will be called into question, so much as the perishing of the material upon which the writing is recorded.

We may also notice here, "Some Observations on Ancient Inks" † which formed the subject of a communication to the Royal Society by Sir *Charles Blagden*. He made experiments on various MSS. on vellum, dating from the ninth to the fifteenth centuries. The ink of some was still quite black, whilst that of others varied from a deep yellowish-brown to a very pale yellow. These were lent him by Mr. *Astle*.

* *Origin of Writing*, 1803, p. 210.
† *Trans. Roy. Soc.*, 1787, lxxvii. (ii.), 451.

He made several experiments, and convinced himself that the ink used in these MSS. was iron-gall. "No trace of a black pigment of any sort was discovered."

He attributes "the greater durability of the more ancient inks" to the more careful preparation of the parchment or vellum; one writing only resisted all the agents which he employed, and that turned out subsequently to be part of a very ancient printed book.

Perhaps the change of which so many writers complain may be more reasonably ascribed to the want of knowledge with regard to the proper proportions of the ingredients employed in the preparation of ink.

In 1857 Mr. *Underwood* * put forward the opinion that the inks in certain writings alleged to have been carbon were probably mixtures of a carbon ink and an iron ink, since some were brown and others yellow in tint, and he considered that this was hardly possible in view of the fact that carbon was supposed to be unchangeable.

This question is among those dealt with by Mr. *Lucas*,† who shows, first of all, that the writing on some old papyri is brown in colour and yet consists of carbon without any iron. This also applies to the ink on many later Egyptian MSS., and it is significant that the change from what was, presumably, black to brown has in some cases only affected parts of a page. The probable explanation of this change is that it is due to the presence of impurities in the carbon, which in the case of inferior qualities was obtained from such materials as carbonised date stones. Traces of tarry oils and iron compounds would thus be introduced into the ink, and it is more reasonable to infer that the slight reaction for iron given by some old carbon inks is due to this cause rather than to a deliberate mixing of two kinds of ink, as suggested by Mr. *Underwood*. For example, an old Arabic account book of 1181 A.H. (A.D. 1767) containing writing, the ink of which gave a faint reaction for iron, but not sufficient to indicate the presence of an iron ink. The brown colour of some of the ink is also to be attributed to a fine coating of a glittering substance, possibly mica, used for drying the ink.

The earliest known instance of the occurrence of an iron ink is in a parchment examined by Mr. *Lucas* (*loc. cit.*), dating back to the 7th or 8th century A.D., which is a century or so earlier than has previously been recorded.

An interesting instance of the use of both a carbon ink and an iron ink in the same MS. is to be found in a portion of the Old

* *J. Soc. Arts*, 1857, p. 67. † *Analyst*, 1922, xlvii., 9.

Testament written in Arabic and bearing the Coptic date 1028 (A.D. 1312). The ink in most parts of the book is brown and has an iron basis, whilst in some pages the ink is black and is carbonaceous. The carbon ink gives slight reactions for iron, but there is no justification for concluding that carbon and iron inks have been purposely mixed.

DOMESTIC INK MAKING.—It is very difficult for us in this twentieth century to realise a time in Britain when the art of writing was a polite accomplishment, only known to a privileged few; when the commercial manufacturer of ink did not, could not exist, for he would have starved through lack of custom. Then it was that the careful housewife would rank it among her duties to make ink, just as she made cordials, and compounded medicines of marvellous origin for the family use; and we may take it for granted that recipes for the manufacture of writing fluids, sympathetic and otherwise, would be handed down, with other nostrums, as precious heirlooms from generation to generation.

We have evidence of this in an interesting volume which was published some years ago by Mr. *George Weddell*, of Newcastle-upon-Tyne.* It is a book of family recipes, which came into his hands by an accident. He has reproduced it in *facsimile*, and it is certainly a most interesting relic of domestic life in the sixteenth and seventeenth centuries. It deals with all kinds of things, good and bad, from recipes for apple pasties to cures for the King's evil. And among the strangely assorted items we find several recipes for making ink. By the kind permission of Mr. *Weddell* we reproduce one of these as a frontispiece; and as few, possibly, of our readers will be able to decipher this sixteenth century writing, the gist of a transcription which Mr. *Weddell* has been good enough to supply, is given in chap. iv.

Another recipe in this delightful old volume stands as follows:—

> Take a quart of fair spring water, one ounce of copperas, two ounces of gall, and four ounces of gum-arabick, mingle them together and let them stand.

Here is another method:—

> Take four ounces of gum arabick, beat small, 2 ounces of gall beat gross. One ounce of copperas, and a quart of the comings off strong ale. Put all these together and stirr them 3 or 4 times a day about—14 dayes then strein it through a cloth.

Then follows this note:—

> I made ink by ye above rect. only putting half ye arabick and as good as ever was used.—K. GREEN.

---

* *Arcana Fairfaxiana Manuscripta*, 1890.

One more recipe from the same source is as follows :—

Mr. Mason, Exciseman, his rect. for making ink, which is very good.
Take a quart of rain or other soft water and put to it 4 ozs. of best blue galls gross by beattin—let it stand warm for 3 days then add 3 ozs. of copperas 4 ozs. of gum ditto roach (rock) allum let it stand 2 or 3 days longer but shake it up 2 or 3 times a day put a little Brandy into the ink. The bottlein it will hinder it from Mouldiness.

There is no date to any of these recipes. Mr. *Weddell*, who has made a study of the different handwritings reproduced in this book, is of opinion that the first of them, our frontispiece, is certainly Elizabethan, and that it was probably written at the end of the sixteenth century by a man past middle age.

A book on handwriting by *John de Beau Chesne* and *M. John Baildon*, printed at Blackfriars in 1571, entitled *A Book containing divers Sorts of Hands*, contains " Rules made by E. B. for his children to learne to write bye." They include directions for making ink. These are quaint enough to deserve quotation :—

To make common yncke of Wyne take a quarte,
Two ounces of gomme, let that be a parte,
Five ounces of galles, of copres * take three,
Long standing dooth make it better to be ;
If wyne ye do want, rayne water is best,
And as much stuffe as above at the least :
If yncke be to thick, put vinegre in,
For water dooth make the colour more dimme.
It hast for a shift when ye have a great nede,
Take woll, or wollen to stand you in steede ;
Whiche burnt in the fire the powder bette small
With vinegre, or water make yncke with all.
If yncke ye desire to keep long in store
Put bay salte therein, and it will not hoare.†
If that common yncke be not to your minde
Some lampblack thereto with gomme water grinde.

In 1609 an iron-gall ink was invented by *Guyot*, and sold on the Pont Neuf, Paris, under the title of *encre de la petite vertu*.‡

In the following century, so much more attention appears to have been given to the manufacture of writing ink, that we find a compound known as " the celebrated Dresden ink " being used in Germany. We give further details as to its composition in Chap. iv.

* Copperas—*i.e.*, iron sulphate.

† A.S. *har*, hoary, grey. Ice. *harr*. In allusion to the grey colour caused by mould.

‡ Blondel, *Les Outils de l'Ecrivain*, 1890, p. 153.

SCIENTIFIC EXPERIMENTS.—The earliest scientific investigation of the chemical reactions between iron salts and an infusion of galls appears to be that of *Robert Boyle*,* who showed that a precipitate was obtained on mixing these chief ingredients of ink. He also described the results of treating ink with various reagents, and showed that similar reactions with iron salts were given by the juices of various plants.

Otto Tachen (*Hippocrates Chimicus*, 1666) attributed the formation of ink to the presence of an alkali in the galls, which neutralised the acidity of the vitriol and formed a black colouring-matter. He showed that when writing was treated with an acid it disappeared, whilst on adding an alkali it again became visible. He also investigated the reactions given by the salts of other metals, such as copper, silver, and mercury, with an infusion of galls.

William Lewis, M.D.,† in 1748, has the credit of being the first to make writing fluids the subject of scientific experiments, and to draw deductions as to the best proportions of the various ingredients required to make a really permanent ink.

Ribeaucourt (1792) ‡ carried out experiments on the same lines as Lewis, but arrived at somewhat different conclusions as to the correct proportions of the constituents.

UNOXIDISED GALL INKS.—The use of dyestuffs such as logwood or indigo to strengthen the colour of the ink, was practised to a small extent during the eighteenth century; but the inks were still of one type—that is to say, the fluids were more or less oxidised before their application to the paper. In the early part of last century, however, a radical change came about in the method of manufacture, and credit for the innovation is claimed by the well-known firm of *Stephens*. Previously to this, the finished ink was exposed to the action of the atmosphere so as to darken it as much as possible, whereby it was rendered more or less insoluble, and would, therefore, for the most part, remain on the surface of the paper. The new process consisted in keeping the ink from oxidation as far as possible, so that the formation of the insoluble pigment would take place within the fibres of the paper; at the same time indigo was added to give the fluid a "provisional" colour.

An unoxidised ink of the same type was patented by *Leonhardi* in Hanover in 1856, a small proportion of madder being incorporated in addition to the indigo. Hence the term *alizarine*, which had

* *Some Considerations touching the Usefulnesse of Experimental Natural Philosophy*, Oxford, 1663.

† *Commercium Philosophico-technicum*, London, 1763, p. 377.

‡ *Ann. Chim.*, 1792, xv., 113.

been accepted as a descriptive title for this type of ink, although *Leonhardi* subsequently omitted the madder as being superfluous. Attempts to employ the more appropriate term "*isatin*" (indigo) to such inks were unsuccessful, and they are still, on the *lucus a non lucendo* principle, sometimes called "alizarine," although the term is fast becoming obsolete. Other manufacturers have seen the advantages of a non-oxidised ink, and the *blue-black* writing fluids are now largely made. In 1891 *Schluttig* and *Neumann* examined eighty-one German inks, and found that all were of the later type—the older kind of ink being obtainable only from a few small makers.

ANILINE INKS.—The next development in the manufacture of ink is found in the use of aniline dyes, not merely for coloured writing fluids, but also for taking the place of the indigo in the black inks. The first British patent for the employment of these dyes as ink was granted to *Croc*, of Paris, in 1861, and it was followed by several others. Thus, under the name of "Stylographic ink" a solution of nigrosine was introduced in 1867, as being specially suitable, on account of its fluidity, for stylographs and fountain pens.

In 1878, at the Paris Exposition, a medal was given to the makers of an aniline ink which was found capable of great resistance to the action of acids, alkalies, and chlorine.

INKS OF STANDARD COMPOSITION.—In 1879 Professor *Koester*, of Bonn, wrote to the German Chancellor, pointing out the danger of using aniline inks for historical documents on account of their instability; and, as a result of this, Prussia passed a law in the same year enacting that only iron-gall inks should be used officially.

In 1888 rules for testing ink were published, and inks were classified according to the way in which they answered to these regulations. Some of these tests were severely criticised by *Schluttig* and *Neumann*.

In 1912 new regulations were made in Prussia, according to which inks were classified into the two groups, "documentary" and "writing inks," the latter being subdivided into (*a*) iron-gall inks and (*b*) logwood and dyestuff inks.

The definitions and methods of examining these different classes of ink are described later.

Several other countries have adopted ink regulations of a similar character. For example, all ink used for official purposes in the State of Massachusetts, U.S.A., must answer to the German requirements.* More recently standard specifications for inks of all kinds

* Information kindly communicated by Dr. Bennett Davenport, Boston, U.S.A.

have been drawn up by the U.S. Government, and within the last few years this example has been followed by the British Government, which now specifies *inter alia* the minimum amounts of iron which must be present in the official inks for record purposes and for fountain pens.

OTHER INKS.—Coloured inks, marking inks, printing inks, and inks for special purposes need only be alluded to, as they are fully dealt with in subsequent chapters. The interesting question of the detection of forgeries by photographic and other means is also considered at length.

SECTION I.

WRITING INKS.

CHAPTER I.

CARBON AND CARBONACEOUS INKS.

As was shown in our preliminary historical sketch, inks having carbon or a carbonaceous compound in a finely divided state for their pigment date back to periods of remote antiquity, though for writing purposes they have to a large extent been superseded, at least in Europe, by inks in which the pigment is more or less in solution.

The inks which may be conveniently considered under this heading comprise (1) Sepia, (2) Indian or Chinese ink, and (3) inks of the type of the ancient writing inks, which contain elementary carbon suspended in a suitable medium.

1. SEPIA.

SOURCE.—The black or dark-brown pigment known as sepia is contained in a secretion formed in a special glandular organ of different species of Cephalopoda, including the common cuttle-fish or squid. The " ink-sac " or " ink-bag," as this glandular organ is popularly called, has strong fibrous walls, and is generally, though not invariably, provided with a separate ejaculatory duct.

Mr. *Martin Duncan*, who had made a study of living members of the Cephalopoda, which he kept in a large tank made for the

purpose, stated in a lecture before the London Camera Club, October 15, 1903, that it is not an easy matter to cause a cuttle-fish to exhaust its stock of ink. And the facility with which it would discharge the liquid upon the least provocation was one of the great difficulties with which he had to deal in prosecuting his inquiries; for a whole tank full of water would be clouded in a few

FIG. 5.—Common Cuttle-fish (*Sepia officinalis*).

seconds, and work had to be suspended until the vessel had been thoroughly cleaned and refilled. He also stated that an exhausted cuttle had the power of renewing the inky secretion in as short a period as a quarter of an hour.

Fig. 5 represents the common cuttle-fish (*Sepia officinalis*) from which the ink is obtained. By the kindness of the Curator of the

Geological Museum, London, we have been able to photograph specimens of fossil Cephalopoda from the Blue Lias in which the ink-bags remain intact. It is a well-known circumstance that this fossil sepia has been more than once ground up with water and found to furnish an excellent ink. This is alluded to in the Bridgewater Treatise by Dean Buckland. In Figs. 6 and 7 the ink sacs are indicated by the white pointers.

Mr. *Henry Lee*, for some time Naturalist to the Brighton Aquarium, writing of this black fluid, says :—*

"The cuttle (sepia) discharges it on the slightest provocation; and this is sometimes very troublesome and annoying when this species is exhibited in an aquarium. The quantity of water its ink will obscure is really surprising. The fluid is secreted with amazing rapidity, and the black injection frequently occurs several times in succession. I have often seen a cuttle completely spoil in a few seconds all the water in a tank containing a thousand gallons."

FIG. 6.—Fossil Sepia.

The extreme diffusibility of the pigment is also referred to by *Ure*,† who states that one part of sepia immediately renders 1,000 parts of water opaque. The cuttle-fish is thus provided with a most effective weapon of defence, which enables it effectually to cover its retreat when attacked by its enemies.

The pigment most highly valued is that obtained from the Mediterranean cuttle-fish, *Sepia officinalis*, and from *S. oloigo*, and *S. tunicata*, though it is also prepared from the ink-sacs of other species. The ink-sacs are removed as soon as possible after the capture of the fish, and rapidly dried to prevent putrefaction. It is a common practice for the fishermen on the South Coast of England to remove the ink-bags of the cuttle-fish, whose flesh they use for their bait, and to keep them in a dried condition until they can dispose of them to the manufacturers. A large amount of sepia is also obtained from Ceylon, where the cuttle-fish are collected by natives for a very low daily wage.

* *Aquarium Notes*—The Octopus.

† *Dict. of Chem.*—Sepia.

MANUFACTURE.—There is good reason for believing that ink manufactured from the pigment of the cuttle-fish was used as a writing-ink by the Romans,* but it is now probably used exclusively in the manufacture of the "sepia" of the artists.

For this purpose the dried ink-sacs are pulverised, and the powder ground up with caustic lye and boiled for thirty minutes. The liquid is then filtered and neutralised with hydrochloric acid, and the precipitated pigment repeatedly washed with water, and dried at a low temperature.

Modifications of this process are used by different manufacturers, the exact details of which are regarded as trade secrets.

The pigment separated from the other constituents by some such process as described above is ground down to an impalpable powder

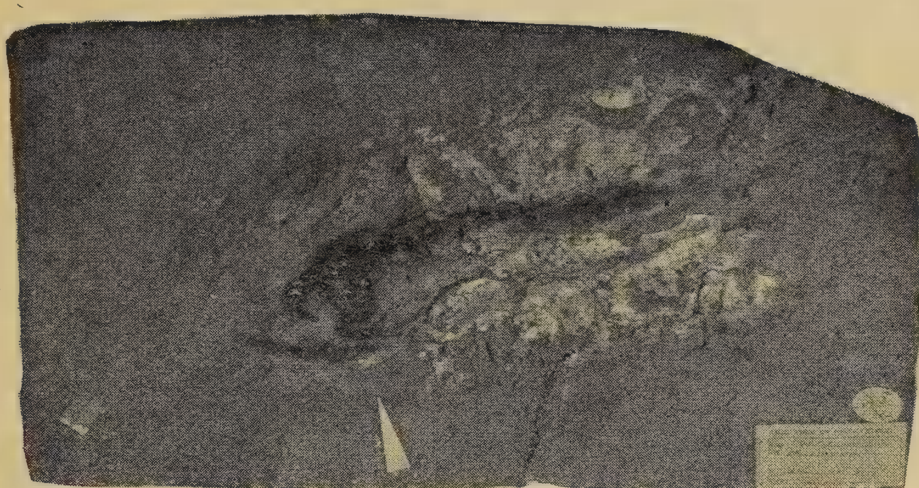


FIG. 7.—Fossil Sepia.

on a marble slab, usually by manual labour. It is then made up into cakes, or is prepared in a moist condition and put up in pans or tubes, or is incorporated with oil for use as an oil paint.

In purchasing the raw material the manufacturer's chief consideration is to see that the ink-sacs are full, not withered. There does not appear to be much variation in the colouring power of different samples of the crude sepia.

CHEMICAL COMPOSITION.—It has frequently been stated,† though without justification, that the pigment of the cuttle-fish consists of finely divided carbon associated with protein substances

* Persius, *loc. cit.*

† *E.g.* in Tomlinson's *Cyclopædia of Useful Arts*, 1854, p. 598.

and calcium phosphate, but it is now known to be a complex organic compound.

Kemp,* who examined the liquid from the ink-sac while in a fresh state, found that it yielded precipitates with alcohol, mineral acids, tannin, and mercuric chloride. It was very viscous, and possessed a peculiar fishy odour, but little taste. He came to the conclusion that it consisted mainly of albumin, with possibly some gelatin.

Shortly afterwards *Prout* † made a chemical examination of the black residue contained in the dried ink-sac. It was a hard, brittle, brownish-black substance with an iridescent lustre. When powdered it yielded a violet-black powder without odour, but with a slightly salt taste. Its specific gravity was 1·640. When digested with water for a long time it yielded a brown solution, giving a brown precipitate with lead nitrate. It was found to contain the following constituents :—Black pigment (*melanin*), 78 per cent. ; calcium carbonate, 10·4 per cent. ; sulphates and chlorides of the alkali metals, 2·16 per cent. ; and mucine, 0·84 per cent.

The melanin was isolated by boiling the black mass with successive portions of water, hydrochloric acid, and dilute ammonium carbonate solution. The residue thus obtained was a black shining powder resembling charcoal in appearance, and emitting a fishy odour when burned. It was insoluble in water, alcohol, or ether, though it remained for a long time in suspension in water. By adding acids or ammonium chloride to the water its separation was accelerated. It was partially soluble in hot potassium hydroxide solution, yielding a brown liquid, from which slight precipitates were obtained with hydrochloric or sulphuric acids, but not with nitric acid. The original pigment was quite insoluble in the two former acids, but dissolved in nitric acid. It was also soluble in ammonium hydroxide, but not in solutions of ammonium carbonate.

A more recent research is that of *Girod*,‡ who made a full analysis of the liquid secreted by the ink-sac of *S. officinalis*. He found it to be odourless, but having a slightly salt taste. When examined under the microscope the liquid was seen to consist of minute corpuscles suspended in a clear serum.

Chemical analysis showed the liquid to consist of 60 per cent. of water ; 8·6 per cent. of mineral matter ; 30·54 per cent. of insoluble organic matter ; and 0·86 per cent. of soluble extractives.

The mineral matter included calcium, magnesium, sodium, potassium, iron, carbonates, sulphates and chlorides, though, curiously, it was free from phosphates.

* Nicholson's *Journ. of Nat. Philos.*, 1813, xxxiv., 34.

† *Annals of Philosophy*, 1815, v., 417. ‡ *Comptes Rendus*, 1881, xciii., 96.

The pigmentary substance was obtained in a pure state by digesting the dried residue for four days with alcohol, and then for four days with ether, to remove the extractives. It was then collected on a filter, washed, and digested with glacial acetic acid to eliminate albuminous substances, then with potassium carbonate to remove mucine, and finally with dilute hydrochloric acid (1 : 10) to free it from the mineral salts.

As thus prepared, the pigment (after drying at 100° C.) was a black homogeneous substance, leaving no residue of ash on ignition. It was insoluble in water, alcohol, ether, and acids, with the exception of nitric acid. It was bleached by chlorine and by bleaching powder, and when heated with soda-lime evolved ammonia.

Its elementary composition was as follows :—Carbon, 53·6 ; nitrogen, 8·8 ; hydrogen, 4·04 ; and oxygen, 33·56 per cent.

Sepiaic Acid.—In 1888 *Nencki* and *Frau Sieber* * obtained an amorphous substance, to which they gave this name, by treating the pigment *melanin* with fifteen times its weight of a 10 per cent. solution of potassium hydroxide. It had the following elementary composition :—Carbon, 56·3 ; hydrogen, 3·6 ; nitrogen, 12·3 ; sulphur, 0·5 ; and oxygen, 27·3 per cent. It was found to be soluble in solutions of alkalis, and was precipitated from its solution by copper sulphate and by ammoniacal zinc chloride.

British Sepia.—Through the kindness of Messrs. *Newman* we have been enabled to examine several ink-sacs of cuttle-fish from Southampton in a dried condition, as received by them. The appearance of these is shown in the accompanying figure (Fig. 8). The general physical characteristics were very similar to those recorded by *Prout* (*supra*), but our specimens had the distinct fishy odour observed by *Kemp* in the case of the fresh liquid, and this became very marked on boiling the powdered substance with water.

The powder contained 17·56 per cent. of moisture, and, on ignition over a low Argand flame, yielded 12·22 per cent. of ash, containing the following constituents :—Silica, 0·28 ; calcium, 1·92 ; magmesium, 1·75 ; chlorine (including other halogens), 1·07 ; sulphuric acid, 1·84 ; total nitrogen, 8·42 per cent.

When treated with boiling water the powder dissolved to a considerable extent, but repeated and tedious extraction was necessary to remove the whole of the soluble matter. The black residue left on the filter amounted to 71·1 per cent. of the original substance, and contained 7·46 per cent. of nitrogen, calculated on the original powder.

The brown solution, when evaporated, left a brown resin-like

* *Chem. Centralbl.*, 1888, xix., 587.

deposit, which, on ignition, gave 4·55 per cent. of ash, calculated on the original substance.

On treating the insoluble residue with boiling 10 per cent. potassium hydroxide, 19·23 per cent. (calculated on the original substance) remained undissolved.

FIG. 8.—Dried Sepia Sacs.

EXAMINATION OF COMMERCIAL SEPIA.—Most, if not all, of the English manufacturers prepare sepia exclusively from the cuttle-fish, but there is reason to believe that a large proportion of the so-called " sepia " of foreign origin is sepia in name only.

A chemical means of distinguishing between genuine sepia and preparations consisting of lamp-black or other forms of carbon incorporated with glue, consists in treating the powdered sample with boiling water until thoroughly disintegrated, filtering the liquid, and thoroughly washing the residue.

In the case of sepia, this residue will contain a large amount of nitrogen, and on ignition will leave a considerable proportion of ash, containing the constituents mentioned in the previous section (p. 21).

Lamp-black preparations, on the other hand, will leave a residue of practically pure carbon, containing only traces of nitrogen, and leaving but little ash on ignition. The whole of the glue, which would cause the finished preparation to show a large proportion of nitrogen, will have been removed by the treatment with hot water and filtration.

The main points to be considered in a manufactured sepia are the colouring power and permanency of the colour.

Sepia was one of the pigments tried in the experiments of Dr. *Russell* and Sir *William Abney* (Chap. vi.), and, to quote the words of the latter : *—" We are apt to look on sepia as one of the most permanent pigments ; as a matter of fact it is fugitive, and those who have examined sepia drawings made in the early part of the century will see there has been certainly a distinct fading in those drawings."

2. Indian or Chinese Ink.

The extreme antiquity of the ink manufactured by the Chinese has already been mentioned in the Historical Introduction. According to ancient Chinese documents cited by *Jametel*,† the earliest ink was a kind of vegetable varnish, and it was not till about the third century B.C. that the solid product prepared from lamp-black and glue was introduced. The province of Kiang-si enjoyed a monopoly of the manufacture, and the ink attained a high degree of perfection, its quality being maintained by special ink inspectors.

This ink has also been prepared in Japan for many hundred years. The province of Omi produced a fine quality known as *takesa*, but the *taikeibuku* of Yamashiro was considered the best. At the present day the best quality of Japanese ink is said to be manufactured in Nara or Matsuda.

LAMP-BLACK.—*Composition :* When carbonaceous products, such as oil, rosin, or tar, are burned with an insufficient supply of air, the oxygen combines with the hydrogen forming water, whilst the carbon is to a large extent deposited in the amorphous form known as lamp-black. The amount of pure carbon in this soot is about 80 per cent., the remainder consisting of oily and resinous substances with inorganic salts, notably ammonium sulphate. For ordinary commercial uses these impurities are not altogether disadvantageous ; but if a purer substance is required, the lamp-black is heated to redness in a closed crucible to carbonise the

* *Journ. Soc. Arts*, 1889, xxxvii., 113.

† *L'Encre de Chine*, d'après des Documents Chinois, traduits par M. Jametel, Paris, 1882.

organic substances, and then digested with hydrochloric acid and thoroughly washed with water to remove inorganic salts, the final product being nearly pure carbon. The purest form of lamp-black is obtained by passing a slow current of turpentine vapour through tubes heated to redness, and igniting the deposit in chlorine to remove the last traces of hydrogen.

Manufacture of Lamp-black: Chinese Method.—The oldest method of which we have any record is that which has been used by the Chinese for centuries.* Various substances have been used as the original source of their lamp-black, such as rice-straw, pine wood, and haricot beans, but these have been for the most part discarded in favour of vegetable oils, and in particular that obtained from the seeds of *Aleurites cordata*, or from tung-oil, which yields a brilliant black ink, deepening in tone with age.

FIG. 9.—Chinese Manufacture of Lamp-black.

The oil is burned in small terra-cotta lamps, which are placed in terra-cotta chambers with a hole to admit air, and having a depression on the top in which water is placed. The smoke is collected in inverted terra-cotta cones with polished interiors, which are fixed above the flame. From time to time the cones are replaced by fresh ones, and the deposited soot

* Jametel, *loc. cit.*, p. 11.

removed by means of a feather, care being taken to reject all oily particles.

Figs. 9, 10, 11 and 12 are reproductions of four of the illustrations copied by *Jametel* from ancient Chinese manuscripts.

In some factories the terra-cotta condensing chamber is replaced by a hollow wooden tunnel, having a hole bored in the wall to act as the ventilating shaft. A range of bricks inside supports the cones, about twenty of which are used at a time.

FIG. 10.—Chinese Manufacture of Ink. Mixing the glue and lamp-black.

The best season for the manufacture of lamp-black is at the end of autumn or beginning of winter. The terra-cotta condensers are placed in a room carefully protected from draughts, which would interfere with the regular deposition of the soot. The cones are examined hour by hour, since delay in changing them causes the lamp-black to assume a yellow tint.

*Julien** states on the authority of Chinese documents that the finest quality of ink is prepared from the lamp-black obtained from sesamé oil, or from tung oil, whilst the soot of pine wood or deal is used for the commoner kinds.

Strips of pine wood about 18 inches in length are burnt in a bamboo cabin, 100 feet in length, which is covered inside and out with paper, and divided into several compartments by partitions, in each of which is an opening for the passage of the smoke. The deposit in the furthest

* *Ann. de Chim.*, 1833, liii., 308.

compartment is the lightest and makes the best ink, whilst that in the first and second compartments is very coarse, and is sold to printers, varnishers, and house painters.

The quality of the lamp-black has a very great influence upon the character of the ink, and the Imperial ink was prepared from the very lightest and purest that could be obtained.

Old European Methods.—Lamp-black is manufactured on a large scale from the resinous impurities obtained as by-products in the manufacture of turpentine, and is also prepared from oil, tar, etc. The initial substance is burned in a furnace with an insufficient supply of air suitably regulated by apertures which can be opened or closed. The dense smoke is conducted through a flue into a cylindrical stone, brick, or cast-iron chamber, the sides of which are covered with sacking or sheep-skin. An iron cone is suspended within the chamber which it fits so exactly that when lowered its edges scrape the suspended sacking and remove the deposited lamp-black (see Fig. 13).

FIG. 11.—Chinese Manufacture of Ink. Pounding the ink.

A small hole in the top of the cone allows the smoke to escape into the chimney of the cylinder, leaving most of its carbon behind. From time to time the suspended sacking is removed, scraped, and replaced.

A more economical method is to conduct the products of com-

bustion first through an iron tube, where oily substances are deposited, and then through a series of iron condensing chambers, where the carbon is deposited, the purest product being obtained from the final condenser. This method of condensing is employed in the manufacture of the finest grades of lamp-black, the source of the smoke being fatty oils burned in lamps.

An impure form of black of bad colour is prepared from certain kinds of coal, and is chiefly used for pitching ships.

Other varieties of black are *Spanish black* from cork; *vine black* from the twigs of the vine; *peach black* from peach kernels; and *German black,* said to be obtained from a mixture of wine-lees, peach kernels, and bone shavings.*

More modern methods of preparing black for printing inks are described in Chap. x.

MANUFACTURE OF INDIAN INK. — The fullest source of information on the Chinese methods of preparing the ink from the lamp-black is still *Chen-ki-Souen's* book as translated into French by *Jametel.* From that we learn that the lamp-black is first sifted into glazed vases, and then dried in paper bags suspended in a dry chamber. The glue is prepared either from fish or from ox-hide, and is used in the proportion of four to five catties † to each pound of lamp-black. If too little glue is used, the ink is blacker, but not so permanent. The

FIG. 12.—Chinese Manufacture of Ink. Rolling the sticks of ink.

* Lewis, *Philosophico-technicum,* 1763, p. 377.

† A catty = 800 grammes.

solution of the glue is poured through a sieve on to the lamp-black, and the paste thoroughly mixed and heated for fifteen minutes in a tightly closed vessel over boiling water. It is next pounded for four hours in a mortar (see Fig. 11), until the mass becomes thoroughly pliable, after which it is mixed with musk and camphor and beaten into long sticks. These are then moulded into cakes weighing about 114 to 140 grammes, and the cakes dried by desiccation in well-burnt ash from rice straw, which is replaced daily by fresh ash. The desiccation takes from one to three or four days or longer, but if the process is continued too long the ink becomes pale and loses its brilliancy.

The following proportions are given as the best for an ink that will become blacker with age * :—Lamp-black from dryandra oil, 10 catties ; old ox-hide glue, 4½ catties ; old fish glue, ½ catty ; extract of sou-mou and another Chinese aromatic plant, 1 catty.

The addition of a small quantity of dried ox-tongue is said to give a violet tint to the ink, and finely powdered vegetable matter is added to produce a bluish tint.

The glue must be white and transparent. It was formerly obtained from various substances, such as rhinoceros' and stags' horns, but is now exclusively prepared from ox-hide or from fish. A decoction of the plant *Hibiscus mutabilis* was formerly used, but according to *Jametel* has long been discarded.

At the present day the only essential difference in the ink produced by different Chinese manufacturers is that different proportions and methods of incorporating the chief ingredients are employed.

The methods of preparing Chinese ink, which are given in a history of China published by *du Halde*, a Jesuit missionary,† in 1735, agree in all essential details with the above account. Lamp-black from pine wood or from oil was mixed with glue or with gum tragacanth and aromatic essences, and the paste pounded, and stamped into tablets, which were finally dried for three to ten days in cold ashes.

In Japan the lamp-black is obtained chiefly from sesamé oil or from pine wood, and is mixed with ox-hide glue in a copper vessel surrounded by another vessel containing hot water. The plastic mass is beaten in wooden moulds into cakes, which, as in the Chinese method, are dried by contact with absorbent ash.

Eisler ‡ describes a method of preparing Indian Ink from animal

* Jametel, *loc. cit.*, p. 28.

† *Description de l'Empire de la Chine*, Paris, 1735, ii., 245.

‡ *Dintefass*, 1770, p. 31.

and vegetable charcoal mixed with milk and thick gum water, and allowed to dry into cakes.

A modern (European) method of preparing Indian Ink consists in grinding up the lamp-black with a dilute solution of potassium hydroxide, so as to form a cream. This is poured in a thin stream into slightly alkaline water, and the deposit is collected, washed with water, dried, and incorporated with a decoction of the seaweed known as Irish moss or carrageen, to which a little musk has been added.

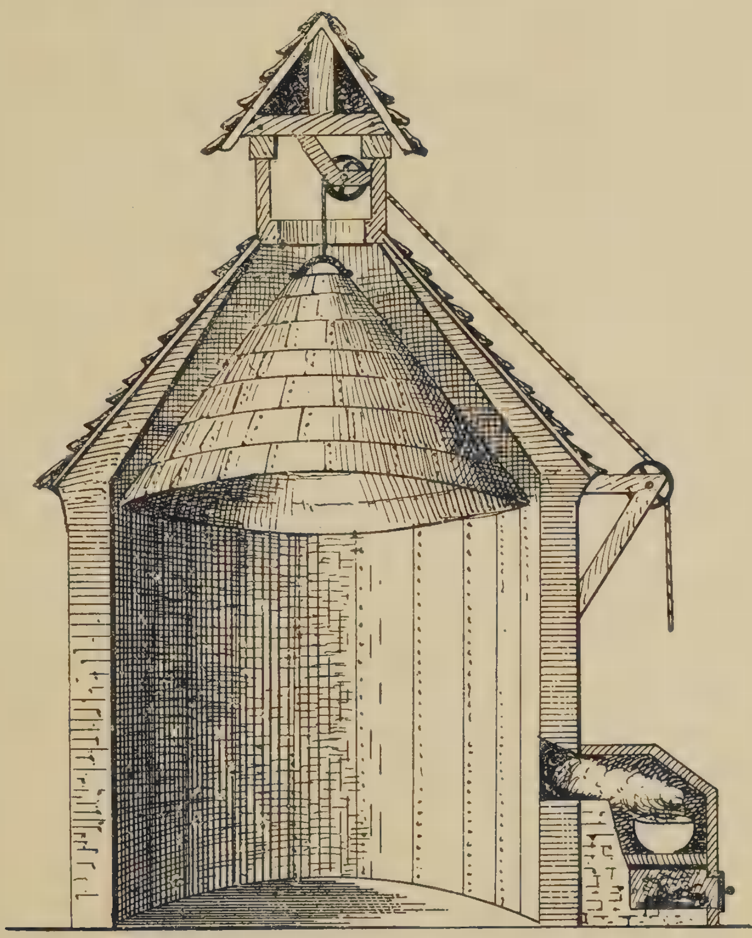


FIG. 13.—European Lamp-black Chamber.

In another process, a solution of gelatin is boiled under pressure for two hours, and then for one hour more, over an open fire until suitably concentrated, and then mixed with lamp-black that has been heated to redness in a close crucible. The object of heating the gelatin is to convert it into the so-called gelatin-peptone, which does not solidify like ordinary gelatin. Indian ink thus prepared does not gelatinise in cold weather.

Merimée * also prepares Indian ink by mixing a strong decoction of galls with a sollution of glue, washing the precipitate with water, and dissolving it in a fresh solution of glue, which is then concentrated to the required consistence and mixed with lamp-black. Dextrin is sometimes used in place of gelatin or glue in the manufacture of cheaper qualities.

Lehner † asserts that he has prepared Indian ink of equal quality to the best kinds obtained from China by the following method:—Petroleum or turpentine oil is burned in lamps to which the supply of air is limited. The smoke is conducted through a zinc tube, 100 feet in length, the inclination of which is slightly upwards. The soot deposited at the remote end of the tube is in a very fine state of subdivision, and requires but little purification to free it from the tarry matter which, if not removed, would cause the ink to have a brownish tint. For this purpose it is first boiled with nitric acid, then washed with water by decantation, then boiled with strong sodium hydroxide solution, and finally washed and dried.

The purified product, consisting of nearly pure carbon, is mixed into a paste with a clear solution of gum, and heated and stirred until evaporated to the required consistence. It is now allowed to cool gradually, a little tincture of musk being added before it quite sets, and is finally kneaded on a flat plate, and pressed into metal moulds, from which the rods are ejected by tapping.

An inferior kind of ink has been prepared by *Lehner* from ordinary soot purified in a similar manner. This method of preparing ink from purified soot was published long before *Lehner's* book appeared.‡

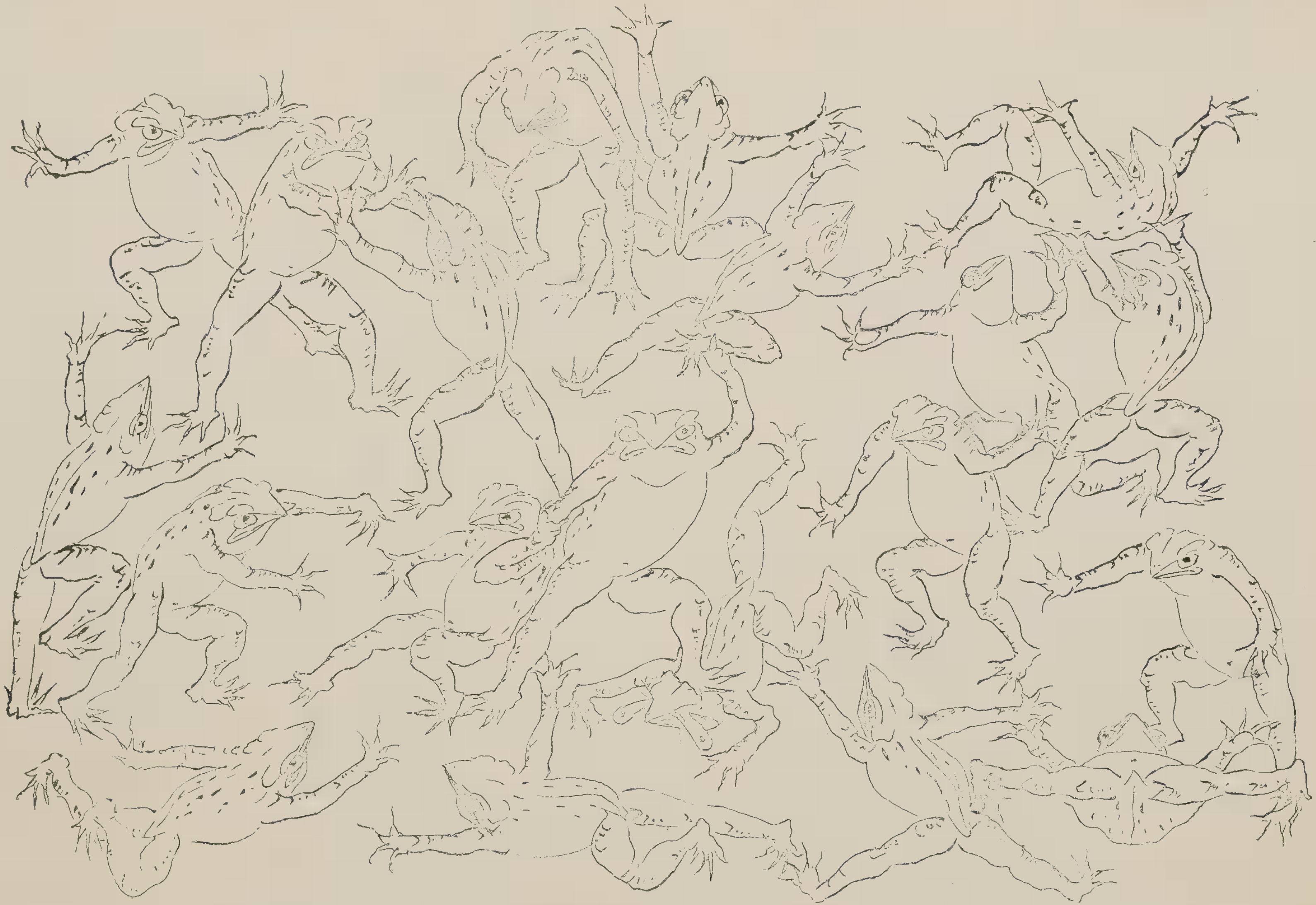
In this country little, if any, Indian ink now appears to be manufactured in the form of cakes. During the war between China and Japan there was a great dearth of the ink, and although some of the largest dealers tried every possible source to obtain a supply, they were unable to do so. From this it would seem that the solid product is now only to be procured from the far East.

This conclusion receives further confirmation from the fact that a large firm dealing in artists' materials now supplies much more of a liquid preparation of lamp-black than of the cakes of Indian ink.

Qualities of Indian Ink.—The ink is imported into England from China in the original boxes, each holding 1 lb. According to the size of the sticks, 8, 20, or 40 may go to the pound, and are spoken of in the trade as "eights," "forties," etc. The sticks are of various forms, some being in squares, some in tablets, and some octagonal. The best qualities of sticks are generally distinguished by being gilt, and

* *Loc. cit.*, p. 197. † *Die Tinten Fabrikation*, 1922, p. 158.

‡ *Dingler's polyt. Journ.*, 1832, xliv., 237.



BRUSH DRAWING IN CHINESE INK BY JAPANESE ARTIST

are stamped with very fine impressions, such as dragons, lions' heads, etc., which denote different qualities well recognised in the trade. They are obtained from Yutshing and Yenshing.

The octagonal sticks are also of very fine quality. The sticks known as "Mandarin" are of fine quality, and are distinguished from ordinary sticks, which have also a lion on the top, by having a finer impression of the Chinese characters on their sides. The commonest kind are in the form of small sticks with white letters on the side.

EXAMINATION OF INDIAN INK.—Among the Chinese the quality of ink is tested by rubbing the tablet on the palette. If only a faint sound is heard the ink is considered to be of good quality (*Si-mo*), but if a loud noise is produced it is regarded as inferior (*Tsou-mo*).

When rubbed with water, Indian ink should yield a uniform liquid, free from coarse particles or flakes. The best Chinese inks have a brilliant violet shade, whilst inks of the second quality are brilliant black, and inferior inks have a yellow tint. A good ink should not lose its intensity or brilliancy on keeping, and should colour paper a brilliant black. Inferior inks lack either blackness or brilliancy, or both.

A practical test of the quality of an ink made from pine soot was recommended by *Julien*.* This consisted in leaving a fragment in water, and noting the time before it rose to the surface. The better the quality the longer the ink was said to remain submerged.

Practical Tests.—We submitted several of the different grades of Chinese ink to practical tests, first of all reducing each to powder, and immersing 0·1 grm. in 10 c.c. of water. It soon became apparent that the better class inks were far more readily diffusible in cold water than were the cheaper kinds, some of the latter hardly colouring the fluid after some hours' soaking. The various samples were then put in a water-bath and raised to the boiling point, but the cheaper grades were still more refractory than the other and required to be rubbed down in a mortar before the particles of carbon were diffused in the liquid. After allowing the containing bottles to rest for an hour, it was found that the sediment of the best samples of ink was of a much finer character than that of the others.

Our next experiment was to test the tinctorial value of the different samples by applying the solutions to Whatman paper, first of all with a full brush, covering a long strip of paper while it was pinned on a sloping drawing-board. Each strip of paper was treated with a different sample of ink, and when the first coat was dry, a second

* *Ann. de Chim.*, 1833, liii., 314.

was applied, not covering the whole of the strip, but leaving a small portion at the end with the first coating untouched. A third, fourth, and fifth coat followed, each falling short of the preceding one, until at the end of the strip a strong black represented the sum of all. A glance at the results at once showed the advantage of employing the better class of ink, for the cheaper kinds were, by comparison, lacking in covering power, and there were present particles of carbon which gave rise to streaks under the brush. The best inks worked far more smoothly than the inferior kinds, and opacity was reached with fewer washes. And from what has been already stated, it will be evident that in the better class of material the labour of rubbing down the pigment from the solid stick is reduced to a minimum. From our examination of the sediment formed in the inks under examination, it would seem that in the better grades lamp-black of much finer quality is employed than is used in the manufacture of the cheaper kinds.

These sticks of Chinese ink are exceedingly brittle, and those rendered unsaleable by breakage are commonly ground up in water to form the liquid ink so much employed by draughtsmen and artists in "black and white."

CHEMICAL COMPOSITION OF COMMERCIAL INDIAN INKS.—The specimens of the four grades of ink submitted to the practical tests described above gave the following results on analysis :—

Indian Ink.	Water. Per cent.	Carbon residue. Per cent.	Nitrogen in residue. Per cent.	Nitrogen in Original Ink. Per cent.	Ash. Per cent.
I. Octagonal stick .	8.16	53.9	0.0	7.74	4.08
II. Lion stick, fine letters . .	7.20	52.53	—	4.87	3.69
III. Lion stick, coarse letters . .	9.93	49.64	—	7.26	4.96
IV. Small stick, coarse letters . .	9.40	57.04	—	6.84	4.01

The fact that the residue left on extracting the soluble substances with hot water is free from nitrogen, affords simple means of distinguishing between Indian ink and pure sepia (see p. 22).

3. Carbon Writing Inks.

ANCIENT CARBON INKS.—The characters on Egyptian papyri and in Latin and Greek MSS. are frequently much darker and more distinct than those written centuries after with iron-gall inks. The latter can be readily destroyed by various chemical agents, such as acids and bleaching agents, and their permanence is also largely dependent on the relative proportion of iron and tannin in the ink, and on the manner in which they have been kept.

Astle, who was Keeper of Records in the Tower of London, and thus had exceptional opportunities of studying MSS. of all ages, found that the black ink used by the Anglo-Saxons in documents of the seventh, eighth, ninth, and tenth centuries had preserved its original intensity much better than that used at later periods, especially in the sixteenth and seventeenth centuries, which was frequently very faint. It was rare to find faded writing in documents before the tenth century. *Astle* * came to the conclusion that this was due to the earlier inks containing carbon; but *Blagden,*† on testing the writing with potassium ferrocyanide, found that iron was present in every instance, although, as was pointed out on p. 10, this was not necessarily a proof that the inks were iron-gall inks.

It is impossible to determine the exact period when carbon inks were replaced by iron-gall inks, though it was probably early in the present era (*cf.* Historical Introduction).

The ink of the Greeks and Latins, like the modern Oriental inks, was a mixture of finely divided carbon with a solution of gum or glue, sufficiently dilute to flow from a reed. In reality, they were only modifications of the Chinese inks described above, and in some cases were even dried before use. Thus *Vitruvius* ‡ states that *atramentum* was prepared from the soot of pitch pine collected on the walls of a marble chamber, mixed with gum (*glutinum*) and dried; and Dioscorides § gives the proportions of soot to gum as three to one.

Evidently the brilliancy of the black deposit and the more fluid character of iron-gall inks led to their gradually superseding carbon inks for writing purposes in Europe, for no mention is made of such inks in mediæval literature.

It is true that *Wecker* in 1582 gave a formula for an *atramentum perpetuum,* but this was really a printing ink consisting of linseed oil and lamp-black, and there is no reference to an aqueous carbonaceous ink in his book or in that of *Canneparius* (1660).

* *Origin of Writing,* 1803, p. 209.
† *Trans. Roy. Soc.,* 1787, lxxvii. (ii.), 451.
‡ *Lib.,* vii., § 10.
§ *Opera,* lib. v., cap. 183.

ORIENTAL INKS.—In Egypt, Turkey, and other countries of the far East, the use of carbon writing inks has never died out, and such inks are still extensively used, with reed pens, for writing in Arabic.

The composition of typical commercial carbon inks, as used to-day in Egypt, has been determined by *Lucas*,* with the following results:—

MODERN EGYPTIAN CARBON INKS.

Sample.	Total Solids. Grms. per 100 c.c.	Ash. Grms. per 100 c.c.
A. Marked : "Best black writing ink, Tabrizy,"	16·1	0·9
B. Stated to be of good quality, . .	11·4	1·9
C. Stated to be of fair quality, . . .	12·0	1·9
D. Stated to be of best quality, Turkish, .	13·5	2·9
E. Marked like "A." Stated to be of first quality, ...	14·6	1·3
F. Marked like "A." Stated to be of second quality, ...	14·1	1·2
G. Stated to be of ordinary quality, . .	8·9	1·2

It is interesting to note that in the case of the best quality of ink the rate of subsidence of the carbon is very slow. For example, best black writing ink, Tabrizy, contained originally 16·1 grms. of total solids per 100 c.c., whilst, after eight years, liquid above the deposit still contained 15·2 grms. per 100 c.c. In the case of a poorer quality, however, the total solids had fallen in the same period from 12·0 to 6·2 grms. per 100 c.c., and these contained no carbon, the whole of which had fallen to the bottom of the bottle. Both of these inks gave slight reactions for iron, evidently due to impurities in the ingredients.

MODERN CARBONACEOUS INKS.—*Lewis* † in 1764 made various suggestions for rendering ink more permanent, some of which are described more fully in Chap. xiv. His principal plan was to add finely divided lamp-black or ivory black to a good iron-gall ink ; but such ink could be bleached by chemical means, to destroy the gall ink, and then washed with water to remove the carbon.

Other chemists have made use of an essential oil, or of a varnish or saponified resinous substance, or a solution of gluten, to retain the carbon in suspension. Of various old formulæ on these lines mention may be made of the following :—

* *Analyst*, 1922, xlvii., 9. † *Loc. cit.*

*Westrumb's Ink.**—Galls, 3 parts; Brazil wood, 1 part; water, 46 parts. Boil until reduced to 32 parts. Strain and add ferrous sulphate, 1½ part; gum arabic, 1¼ part; indigo, 1¼ part; and lamp-black, ¾ part.

Close's Ink.†—Powdered copal (25 parts), in lavender oil (200 parts), mixed with lamp-black (2½ parts), and indigo (½ part). If too thick, the ink was thinned with turpentine.

Sheldrake's Ink.‡—A mixture of asphalt, dissolved in turpentine, with amber varnish and lamp-black. The whole question of the best means of rendering writing safe from attempts to remove it is discussed in Chap. xiv.

* Nicholson's *Journ. of Nat. Philosoph.*, 1802, iv., 479.
† Nicholson's *Dict. of Chem.*, 1820. ‡ *Ibid.*

CHAPTER II.

RAW MATERIALS FOR INKS.

CONTENTS.—**I. Tannin Substances—Galls**—Origin—Aleppo galls—Chemical composition—Chinese galls—Chemical composition—Japanese galls—Acorn galls—Oak-apple galls—Other galls—**Tannins**—Classification of tannins—Suitability of tannins for ink-making—**Chestnut bark and wood**—Chestnut extract—Chestnut tannin—Ink from chestnut wood—**Sumach**—Sumach tannin—Ink from sumach—**Divi-divi**—Divi-divi tannin—Ink from divi-divi—**Myrobalans**—The tannin of myrobalans—**Valonia**—The tannin of valonia—Ink from valonia—**Oak-bark tannins**—Reactions of oak tannins—Amount of tannins in oak bark—Ink from oak bark—**Gallotannic acid**—Fermentation of gallotannic acid—Properties—**Gallic acid**—Properties—Reactions distinguishing between gallotannic and gallic acids—**II. Iron Salts—Ferrous sulphate or Copperas**—Preparation—Properties—Double sulphates—**Ferric chloride—Ferric sulphate chloride.**

GALLS—I. TANNIN SUBSTANCES.

ORIGIN.—Curious abnormal excrescences, known as galls, are frequently formed upon the branches, shoots, and leaves of plants and trees, and notably upon the oak. They are produced by the introduction of a foreign organism which sets up an irritant action within the plant, resulting in the development of a growth which, possibly, stands in some form of symbiotic relationship to the causal organism. For example, many of the various kinds of galls on oak trees, typified by the common oak marble, are produced by the females of certain species of insects, of which the best known are the hymenopterous gall-wasps (*Cynipidæ*), which puncture the young tissues and deposit their eggs. Under this stimulus the plant juices accumulate at the point of puncture, and a gall is gradually formed, which serves as the home of the larva. It is possible that some virus injected simultaneously with the egg plays a part in the development of the gall, but the main essential appears to be the presence of the living larva. Should the egg of the insect perish from any cause no gall is formed, or if the larva dies the gall ceases to grow.

Other kinds of galls are produced by the action of mites, aphides (Chinese galls), coleoptera, mould fungi, or bacteria. Some idea of the great variety of these growths may be gained from the fact that Houard (1909) has catalogued no fewer than 6,279 galls occurring in Europe and the Mediterranean countries.

Galls vary greatly both in size and shape, some—*e.g.*, the Californian " flea seed," being very minute, whilst others, like the large galls on the roots of certain oaks, are several inches in diameter. Some galls are round and smooth, like the English oak-apples; others, like the Aleppo galls, are crowned with protuberances; and others again assume fantastic forms, as in the case of the " artichoke gall " found on certain French oaks, the curious British galls shown in Figs. 15, 16, and 17; the Chinese and Japanese galls (Figs. 21 and 22); and the bedeguars (" moss apples ") produced by various species of *Rhodites* on rose bushes. The forms and colours of the different kinds of galls are remarkably constant, and afford a means of distinguishing between the insects, often of very similar appearance, that produce them.

FIG. 14.—Oldest known drawing of a gall, from *Hortus sanitatis* (end of fifteenth century).

In the majority of cases galls contain only one larva, and are described as " monothalamous," whilst others afford shelter and food to a colony of larvæ, and the term " polythalamous " is applied to them. Typical examples of these are the normal Aleppo galls and Chinese galls.

References to different kinds of galls are to be found in various classical and early medical writings, such as those of Hippocrates and Dioscorides, and Pliny (*Hist. Nat.*, xxiv., 5) gives some account of the " moss gall " of the rose and of several kinds of oak galls. The naturalists of the middle ages (*Albertus Magnus*, 1193-1280) and *Megenberg* (1309-1337) also give descriptions of the more common galls, and the oldest work on herb lore, *Hortus sanitatis*, which appeared about the end of the fifteenth century, gives a drawing of the oak gall of *Cynips*

tinctoria, which, according to *Küster*,* is the oldest drawing of a gall extant (see Fig. 14).

It was not until *Malphigi* published his "Anatomy of Plants" (1675 and 1679) in London that any detailed study of the morphology and biology of galls was available. This work, which is characterised by its keen observation, was written in Latin; it laid the foundation of the modern scientific investigation of galls.†

In abnormal cases an oak gall, such as the British oak marble, may contain a large larva in the central chamber and a number of much smaller larvæ (*inquilini*) distributed round the pericarp, in which they have been deposited after the development of the gall

FIG. 15.—Sections of British gall, showing true larva and inquilines.

(see Fig. 15). This phenomenon was noticed by *Malphigi* in his *Anatome Plantarum* (1679).

When two galls of the same kind develop sufficiently close to one another they exert a reciprocal influence, so that they coalesce and form a double gall, as is shown in Fig. 16; instances may also occur of three or four galls being thus united into a single individual.‡

* *Die Gallen der Pflanzeu*, Leipzig, 1911.

† A German summary of Malphigi's classical work by Möbius was published in 1901. (Englemann, Leipzig.)

‡ *Cf.* Connold, *British Oak Galls*, 1908, p. 160; E. A. Ormerod, *The Entomologist*, 1878, xi., 82.

ALEPPO GALLS.—The ordinary *nut-galls* of commerce are commonly known as *Aleppo*, *Turkey*, or *Levant galls*. They are produced by a gall wasp, *Cynips tinctoria* (*Cynips kollari*), upon the branches of a small oak, *Quercus infectoria* (a variety of *Q. lusitanica*), which is abundant on the Syrian coast, and to the east of the River Jordan. The insect pierces its way out of the gall after five or six months, and the uninhabited galls are then known as *white galls*, from their pale colour. These usually contain considerably less tannin than galls which still enclose the larva, and have, therefore, a smaller commercial value. The best galls are selected ahead and

FIG. 16.—British double oak-marble gall.

FIG. 17.—British oak gall. Autumn condition of oak-apple due to *Teras terminalis*.

FIG. 18.—British gall. (The "twig gall" produced by *Andricus inflator*.)

harvested before the insect escapes, and from their colour are known as *blue* or *green* galls.

The value of a given sample of galls depends to some extent upon the proportion of white galls it contains. Hence, fraudulent

attempts have sometimes been made to close the holes left by the insect, and so make the galls to appear still to contain the larva.* A section of the nut would readily detect this fraud (see Fig. 21). Aleppo galls vary somewhat in size, but usually average from 8 to 15 mm. in diameter. They are globular or pear-shaped, and are crowned with numerous tubercles (Fig. 19). The colour ranges from greenish-black to pale yellowish-green, whilst the interior is pale brown or yellowish-green.

The appearance of *white* galls is shown in Fig. 20, and in section in Fig. 21, which also shows the small canal through which the insect made its way to the surface.

When a thin section of an inhabited gall is examined under the microscope it is seen to consist of an external layer of small cells, forming a sort of bark; beneath these are cellular layers of parenchyma, some of the cells containing tannin and chlorophyll; then

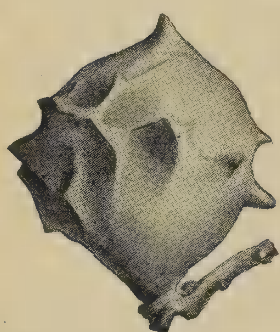


FIG. 19.—Green Aleppo gall.

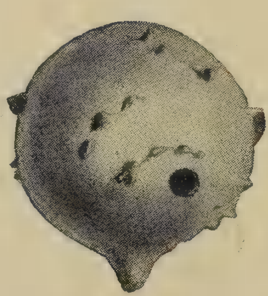


FIG. 20.—White Aleppo gall.

FIG. 21.—Section of white gall.

come radial cells surrounding the central cavity, in which lies the larva in the midst of an alimentary mass.

Smyrna galls appear to be a commercial variety of Aleppo galls, being somewhat larger and darker in colour, and often containing a larger proportion of white galls.

Tripoli or "*tarablous*" *galls* are of less value than Aleppo galls.

Chemical Composition.—By treating 500 grains of the best Aleppo galls with distilled water, *Davy* † obtained an infusion of specific gravity 1·068. It contained 185 grains of solid matter, consisting of 70·27 per cent. of tannin; 16·75 per cent. of impure gallic acid; 6·48 per cent. of gum and other extractives; and 6·50 per cent. of salts of calcium and other metals. From the results of tannin estimations made by later chemists there appears to be little doubt that Davy had not extracted the whole of the soluble constituents

* Allen, *Commercial Organ. Anal.* † *Trans. Royal Soc.*, 1803, xciii., 233.

of the galls, for, on this basis, the insoluble woody fibre amounts to 63 per cent. of the total substance.

In 1845 *Guibourt* * made a very exhaustive examination of Aleppo galls; and his results, still quoted in text-books, are as follows:—Tannin, 65·0; gallic acid, 2·0; ellagic and luteogallic acids, 2·0; chlorophyll, 0·7; brown alcoholic extract, 2·5; gum, 2·5; starch, 2·0; woody fibre, 10·5; sugar, protein, potassium and calcium salts, 1·3; and water, 11·5 per cent.

A later, though less complete, analysis is that of *Watson Smith*, who found Aleppo galls to have the following composition:—Tannin, 61·65; gallic acid, 1·60; woody fibre, 15·68; water, 12·32; and colouring matter and loss, 8·75 per cent.

Büchner † obtained the following amounts of extractive matter by treating the powdered galls with different solvents:—

	Per cent.
Substances extracted by ether, ...	77·0
,, ,, by ether and alcohol, . .	80·4
,, ,, by cold water, . . .	86·5

Hinrichsen ‡ gives the following figures as the average amounts of tannin in European galls:—Morean, about 30; Istrian, over 40; German or Central European, about 15; and Knoppern, up to 35 per cent.

Samples of commercial nut-galls analysed by the writer's colorimetric method, as described in Chap. iii., gave the results in the following table:—§

COMPOSITION OF ALEPPO GALLS.

(*Factor* = 1·85.)

	Moisture. Per cent.	Total extract. Per cent.	Tannin. Per cent.	Gallic acid. Per cent.	Total pyrogallic equivalent Per cent.
1. Blue galls, old, . .	10·25	80·4	53·5	11·2	26·5
2. ,, ,, . .	11·01	74·0	61·9	1·5	23·2
3. ,, new, . .	10·85	86·4	79·5	7·0	33·3
4. ,, ,, . .	13·05	86·4	77·5	3·5	28·8
5. Green galls, . .	11·00	73·4	61·8	2·5	23·9
6. White galls (same lot), .	10·72	72·4	52·9	7·4	24·0
7. Roasted galls, . .	10·51	59·6	37·6	20·0 (=13·3 Pyro.)	26·6

* *Archiv. der Pharm.*, 1846, li., 190; *Hist. Nat. des Drogues*, 1849, ii., 286.
† *Rep. f. Pharm.*, 1851 (3), vii., 313.
‡ *Die Untersuchung von Eisengallustinten* (1909), p. 21.
§ *Analyst*, 1923, xlviii., 11.

The method used was to take about twelve galls from a sample and to crush them to a coarse powder, which was then thoroughly mixed. Five grammes of the mixture were boiled for an hour each time, with successive portions of about 150 c.c. of water, the extracts filtered, and the whole made up to 500 c.c. Ten c.c. of this 1 per cent. extract were diluted to 100 c.c., and 1 c.c. of this 0·1 per cent. extract compared in the usual way with the standard gallic acid solution.

If the factor 2·1 were used for converting the gallic acid equivalent of the precipitated tannin into tannin, the amount of the combined tannin and gallic acid would in some cases exceed that of the total extract.

If, however, we deduct from the total solids in the extracts from new galls the amount of anhydrous gallic acid found and the average amount of gum in nut galls (2 per cent.), and divide the difference by the gallic acid equivalent of the precipitated tannin, we get in the case of the new galls (3 and 4) factors of 1·82 and 1·96 respectively. The average of various estimations gave 1·85.

For comparing the tinctogenic values, however, it is advisable to express the total results in terms of pyrogallol. After reporting on Nos. 3 and 4, the author was informed that the price asked for No. 3 was 13 per cent. higher than for No. 4. Tinctogenically it was worth nearly 16 per cent. more.

The White Galls (No. 6)—*i.e.*, those from which the larvæ had escaped, leaving an open channel, were picked out of the consignment of green galls No. 5.

From the tanning point of view the lower value attributed to white galls is justified, but from the tinctogenic point of view much will probably depend upon the extent to which the oxidation has proceeded within the galls. In the case of this particular sample it will be seen that, while the tannin had been reduced, the gallic acid had increased, so that the total tinctogenic value was the same in each case.

Some light may be thrown on this question by a comparison of the results given by English oak-marble galls at different stages of their growth (see p. 51).

Roasted Galls.—Galls are sold, not only in their natural state or in a crushed condition, but also after being roasted. This process of roasting, which is done by a rule-of-thumb method, causes the galls to become friable and dark brown in colour ; after the treatment they yield a darker ink than in the raw condition. This fact is well known, but, so far as the writer is aware, no explanation has been given of its cause.

When galls are heated to 220° C. the gallotannin is decomposed, first with the formation of gallic acid and then of pyrogallol, some of which separates as a sublimate.

The decomposition appears to be far from quantitative, for in two experiments in which 0·1 gramme of gallotannin was heated for 30 minutes (one at 220° C. and the other up to 300° C.), the amounts of sublimate collected were only equivalent colorimetrically to 0·85 and 0·65 per cent. of pyrogallol, respectively.

It is mentioned later (p. 83) that some years ago Schluttig and Neumann made a series of experiments upon the stability to sunlight and air of colour washes on paper of the iron compounds of various trihydroxylated substances. They found that the gallotannin compound faded to pale yellow, the gallic acid to grey, and the pyrogallol compound to dark brown, and expressed their surprise that gallotannin, with its accepted composition of a digallic anhydride, should not have exceeded the other two in depth of colour and permanence.

The facts brought out (p. 99) will explain why pyrogallol comes first and gallotannin last in the series; and, if we assume that the production of pyrogallol is the cause of the increase in the blackness of ink from roasted galls, we ought to be able to obtain some evidence of this by the colorimetric method.

A reference to the results given in the table (No. 7), p. 41, shows that this is the case. Roasting the galls reduces the amount of soluble extract and gallotannin, but greatly increases the non-tannin colorimetric equivalent.

CHINESE GALLS.—The curious variety of galls exported from China is not formed by a gall-wasp like most of the commercial galls, but is produced by a small aphis (*Schlechtendalia chinensis*) upon the leaf, stalks, and shoots of *Rhus semialata*, a tree growing abundantly in sandy places in Northern India, China, and Japan.

The aphis is about $\frac{1}{30}$ of an inch in length by about $\frac{1}{40}$ in breadth at the base of the abdomen, which gradually widens out from the thorax (see Fig. 25).

The gall is at first dark green, and gradually changes to yellow before the larva escapes through the walls bursting open, the Chinese peasants collecting them shortly before the change takes place. The aphides are killed by exposing the galls in osier baskets to the action of steam.

The gall is naturally covered with a light powder termed "salt powder" by the Chinese, and used by them for flavouring soup and as a medicine.* As imported into Europe, the galls are pale

* Pereira, *Pharm. Journ.*, 1844, iii., 384.

grey in colour, and have a horn-like appearance, and a curious odour resembling that of freshly tanned leather. They vary greatly both in size and in form, but a characteristic shape is shown in Fig. 22. They have a horn-like texture, and, when broken open, present a hollow interior containing a little chalk-like dust with darker particles, which, when examined under the microscope, are seen to be mainly dried aphides.

According to *von Rebling*,* an average-sized gall contains more than 3,000 aphides, and by treating the debris with warm water these swell up to about $\frac{1}{24}$ of an inch in size.

The writer is indebted to Mr. T. J. Ward for the accompanying photo-micrograph of the dust contained in a commercial gall (Fig. 23). This dust was soaked in potash to cause the aphides to swell up and give some idea of their original appearance.

Du Halde † gives a description of these galls, which, he states, are termed *ou-poey-tse* by the Chinese and are used by them in the preparation of various medicinal compounds. He also states that their formation is due to a small insect.

FIG. 22.—Chinese gall.

Chinese galls were first imported into Europe in the eighteenth century under the name of "Oreilles des Indes," but they did not become a regular article of commerce until about 1850. They are now largely used in Germany and America as the raw material for the manufacture of gallotannin, and they form one of the principal and cheapest tannin materials for the manufacture of ink. In fact, according to *Dieterich*,‡ gall inks are now prepared from them almost exclusively in Germany. In this country they are not used to the same extent as Aleppo galls.

Büchner § compared their commercial value with that of ordinary gall-nuts. In 1851 good average blue Aleppo galls cost 100s. to 105s. per cwt., whilst Chinese galls fetched 65s. to 68s. per cwt. Thus, taking into account the fact that the tannin material in Chinese galls is more readily soluble than that in Aleppo galls, their value was from $1\frac{1}{3}$ to $1\frac{1}{2}$ times more than that of Aleppo galls.

* *Archiv. f. Chem.*, 1855, cxxxi., 280.

† *Description de l'Empire de la Chine*, 1735, p. 496.

‡ *Pharm. Manual*, 1897, p. 680.

§ *Rep. f. Pharm.*, 1851 (3), vii., 329.

Chemical Composition.—Specimens of Chinese galls were examined in 1817 by *Brande*,* who found them to yield 75 per cent. of soluble matter to cold water, the residue consisting of woody fibre with 4 per cent. of resinous matter soluble in alcohol. The residue from the aqueous extract was found to consist mainly of tannic acid with a little gallic acid.

From the absence of extractives (gums, etc.), *Brande* concluded that these galls would not be suitable for tanning purposes, and, in fact, he found that leather prepared with them was very brittle when dried. On the other hand, he found this property rendered them particularly suitable for the manufacture of ink, and the

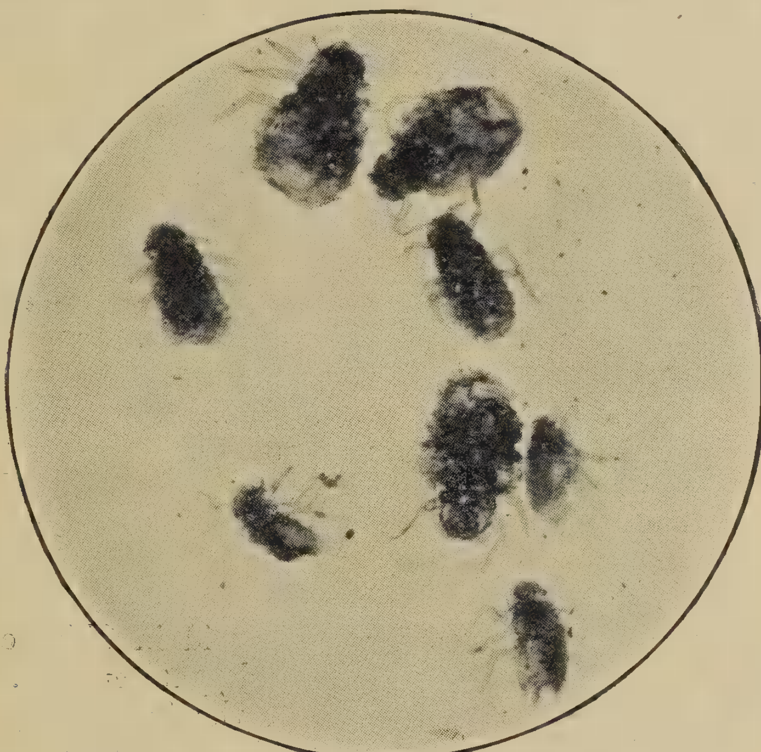


FIG. 23.—Aphides in dust from Chinese gall.

ink prepared from them proved to be less liable to become mouldy than that from ordinary galls.

In 1849, *Stein* † described a variety of Chinese galls as possessing an odour of tobacco, and containing the following constituents :—Ash, 2·00; tannic acid, 69·14; other tannins, 4·0; green saponifiable fat, 0·97; starch, 8·20; woody fibre, 4·9; and "inert" matter, 12·96 per cent.

* *Trans. Roy. Soc.*, 1817, cvii., 39.
† *Dingler's polyt. Journ.*, 1849, cxiv., 433.

The tannin was completely extracted by boiling the powdered galls three times with eight times their weight of water. It was regarded by *Stein* as identical with the tannin of ordinary galls. This is not borne out by modern investigations (see p. 75).

The ash contained potassium, calcium, magnesium, iron, chlorine, and phosphoric acid.

Bley's * results are similar to those of *Stein*—viz., Gallotannic acid, 69·0; resin and fat, 3·0; gallic acid, extractives and proteins, 4·0; starch, 7·35; woody fibre, 8·65; and water, 8·0 per cent.

Büchner's † analysis in 1851 gave the following results:—Tannic acid, 76·97; fat and resin, 2·38; extractives soluble in water, and some salts, 0·89; gums and salts, 5·94; and starch, woody fibre, and mineral matter, 13·82 per cent., calculated upon the substance dried at 100° C.

When extracted with ether these galls yielded 79·35 per cent. of soluble matter, of which 76·97 per cent. (on the original substance) dissolved in water. *Büchner* was unable to confirm *Stein's* conclusion as to the presence of other tannins in addition to gallotannic acid. He also came to the conclusion that the tannic acid was identical with that of oak-bark, and that gallic acid was only present in the galls in very small proportion. The mineral matter was found to consist principally of magnesium phosphate.

Tannic Acid.—The proportion of tannic acid found by *Stein*, *Bley*, and *Büchner* is substantially the same when calculated upon the dried substance—viz., *Stein*, 79·43 per cent.; *Bley*, 75 per cent.; and *Büchner*, 76·97.

Viedt ‡ gives the proportion of tannic acid in Chinese galls as about 72 per cent., whilst *Ishikama* § found 77·4 per cent.

A sample analysed by the writer gave the following results:—Moisture, 10·70; ash, 1·43; and substances soluble in water, 78 per cent. The tannin determined by *Procter's* method was only 68 per cent.

On the other hand, two samples obtained from different sources were recently examined and yielded much lower extracts, as shown in the following table, in which the amounts of tannin were estimated by *Mitchell's* colorimetric method:—||

* *Archiv. d. Pharm.*, 1850, cxi., 297.
† *Loc. cit.*, p. 323.
‡ *Dingler's polyt. Journ.*, 1875, ccxvi., 453.
§ *Chem. News*, 1880, xlii., 274.
|| *Analyst*, 1923, xlviii., 13.

COMMERCIAL CHINESE GALLS.
(*Factor* = 2·1.)

	Moisture. Per cent.	Total extract. Per cent.	Tannin. Per cent.	Gallic acid. Per cent	Total pyrogallol equivalent Per cent.
Chinese galls I., . .	9·71	63·2	60·9	4·0	22·0
,, II., . .	11·01	63·8	52·7	6·4	21·0

It is interesting to note that the total tinctogenic value of these particular Chinese galls was lower than that of good nut-galls. This was contrary to the commonly accepted belief. It is possible, however, that these galls, although sold as Chinese galls, were in reality the Japanese variety (*vide infra*).

Viedt (*loc. cit.*) asserts that Chinese galls do not contain the necessary ferment (*i.e.*, enzyme) for the conversion of the gallotannic acid into gallic acid, and that, therefore, they cannot be used for the manufacture of ink unless a small proportion of Aleppo galls or of yeast is added to the infusion.

The writer is unable to confirm *Viedt's* statement, which is also altogether at variance with the results obtained by *van Tieghem*,* who has clearly demonstrated that the conversion of gallotannin into gallic acid is brought about, not by a pre-existing enzyme, but by the action of certain mould fungi.

Ink was prepared by adding ferrous sulphate to a decoction of Chinese galls, without any addition of either yeast or other galls, and this behaved just like ordinary gall ink, giving a writing which rapidly became black on exposure to the air.

Moreover, insoluble deposits formed on exposing the ink to the air, and these deposits contained 6·86 to 7·56 per cent. of iron, results very near to those obtained with ink from gallotannin or ordinary Aleppo galls.

JAPANESE GALLS.—These galls are closely allied to the Chinese galls, and are frequently stated to be identical with them. They are produced by *Schlechtendalia chinensis*, or an allied aphis, upon the shoots of *Rhus japonica* (Siebold) or *Rhus javanica* (Murray). (See Fig. 23.) They must, however, be regarded as at least a distinct variety, and in fact are so recognised in commerce, though for ink manufacture the two varieties are used indiscriminately. According to *Procter*,† the Japanese galls are smaller and paler,

* *Comptes Rendus*, 1867, lxv., 1091. † *Text-book of Tanning*, p. 28.

and are usually more esteemed—*i.e.*, from the tanning point of view.

Ishikama * states that considerable quantities of Chinese galls were formerly imported into Japan, but that in 1880 only the native product was used. The Japanese galls (*Kibushi*) are plucked from the trees between July and September, and are placed in boiling water in wooden tubs for thirty minutes, and then dried in the sun for three to four days. They are stored in warehouses in Kiyoto, often for several years, before being used. The reactions given by the tannin they contain are stated to be identical with those of ordinary gall-nut tannic acid.

The amount of tannin estimated by the permanganate process in seven samples of different ages up to eight years ranged from 58·82 to 67·7 per cent. The old galls were very brittle, and gave much darker decoctions than the fresh galls, but did not contain less tannin.

The commercial Japanese galls that the writer has had the opportunity of examining undoubtedly differed both in size and shape from the Chinese product, were also softer, and had very much thinner walls. A typical Japanese gall is shown in Fig. 24. These galls contained 10·46 per cent. of moisture, 1·96 per cent. of mineral matter, and yielded 50 per cent. of soluble substances when boiled for three hours with successive portions of water.

Mr. *R. M. Prideaux*, who has kindly made a microscopical examination of the debris in some of these Chinese and Japanese galls, states that the two aphides are not demonstrably of different species. Those from the Chinese galls were uniformly smaller than those from the Japanese galls, and lacked the rudimentary wings of the latter; but it would be necessary to follow out the entire life-history of both in the growing galls before being able to determine with any certainty the *specific* value of the differences observed in the dead debris. (See Figs. 25 and 26.)

FIG. 24—Japanese gall.

ACORN GALLS (*Knoppern*).—These galls, also known as *Piedmontese galls*, are produced by the female of *Cynips calicis* on the cupules of different oaks (*Q. pedunculata, Q. sessiliflora*, etc.), in the forests of Austria and Czecho-

* *Chem. News*, 1880, xlii., 275.

Slovakia, especially in Dalmatia, Slavonia, and Croatia. It is in the form of a hollow truncated cone with radial ribs, usually about 12 mm. in diameter at the base, and about 4 mm. at the top. The cell which contains the larva is near the base of the gall. The interior is spongy, and has a spheroidal chamber containing the larva in the centre. This gall is the same as the *pomme de Chêne* of *Réaumur*.*

The galls are collected from August to October, after they have fallen from the trees, and are sold either whole or in the form of powder, or as an extract. They contain less than 45 per cent. of tannin, which, according to *Löwe*,† is the same as that of other galls, giving analytical results corresponding with the formula, $C_{14}H_{10}O_9$.

Eitner ‡ made an examination of the Knoppern collected in 1884 in different districts of Austria, and found them to contain

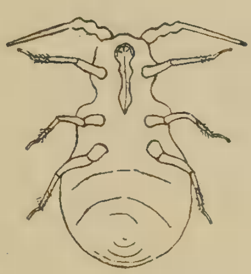


FIG. 25.—Aphis from Chinese gall. × 18.

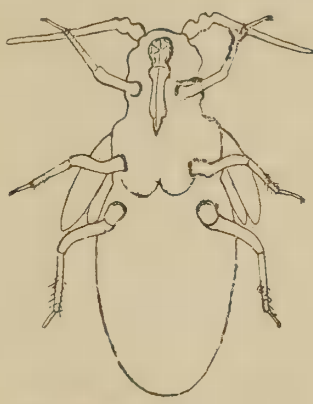


FIG. 26.—Aphis from Japanese gall. × 18.

about 12 per cent. of moisture, and from 23·94 to 35·02 per cent. of tannin.

Knoppern galls are sometimes used in the manufacture of ink, though, according to *Viedt*,§ their use was not common, probably owing to their comparatively low proportion of tannin. *Lehner*,‖ however, states that they are a regular article of commerce in Hungary, the main source of supply being the Bakouyerwald between the Neusiedlersee and the Plattensee, where they are collected in August. According to the same authority, Knoppern are also exported in considerable quantities from Asia Minor, as an article of commerce distinct from nut-galls.

* *Dict. des Sciences Medicales*, art. "Galles."
† *Zeit. anal. Chem.*, 1875, xiv., 46.
‡ *Dingler's polyt. Journ.*, 1885, cclv., 485.
§ *Dingler's polyt. Journ.*, 1855, ccxvi., 453.
‖ *Die Tinten-Fabrikation*, Vienna, 1922, p. 20.

Aleppo galls (*q.v.*), produced on the *Quercus infectoria* of Asia Minor, are somewhat similar to Knoppern, but are more spherical, and have the tubercles round the centre instead of at the top.

OAK-MARBLE GALLS.—The common galls known in England as *oak marbles*, or frequently, though incorrectly, as *oak apples* (see Fig. 16), are produced by a species of *Cynips* (*C. Kollari Hartig* or *C. lignicola*) on the branches of the oak, *Quercus robur*, and appear to be closely allied to, if not identical with, galls formed on that oak throughout Central Europe.

They are usually spherical (see Fig. 27), and of a light greyish-green or reddish colour.

These galls were unknown in England prior to 1834, in which year their appearance was recorded near Exeter, and they thus became known as *Devonshire galls.* In the early years of last century large quantities of Aleppo galls were used for dyeing the cloth manufactured near Exeter and Tiverton, and it is suggested by Connold * that possibly *C. Kollari* was introduced for experimental purpose. From that time these galls gradually spread over other counties, until they became one of the commonest British galls.

British galls contain very much less tannin than Aleppo galls, and generally less than Knoppern. *Braithwaite* † obtained only an insignificant amount from Devonshire galls, but did not state what method of estimation he employed.

In 1856 *Vinen* ‡ made an examination of the galls produced by *Cynips Kollari*, after the escape of the insect. 100 parts of the galls digested with ether and water gave 26·74 parts of extract, containing 17 parts of tannic and gallic acids. According to *Vinen* these galls were at that time used in Devonshire for the manufacture of ink.

In 1847-48 the oaks in East Devonshire were abnormally infected with *Cynips Kollari* (Fig. 27), and the galls also appeared suddenly in 1860 in great quantities in the woods to the North of London. According to *D'Urban*,§ these galls contained a considerable amount of tannin and made excellent ink.

As there was considerable doubt as to the commercial value of British galls, and conflicting statements had been published as to the amount of tannin present, *Judd* made a series of experiments on galls at different seasons, the tannin being precipitated in each case by means of alum and gelatin. He found that old galls hanging on the trees in December contained on the average 15·97 per cent. of tannin, whilst mature imperforated galls gathered in August

* *British Oak Galls*, p. 102.

† *Pharm. Journ. Trans.*, 1855, xv., 544.

‡ *Ibid.*, 1856, xvi., 137.

§ *Ibid.*, 1863, xxii., 520.

contained on the average 17·65 per cent., and half-developed and shrivelled galls 13·44 per cent.

An ink of average quality was prepared from the old perforated galls.

An analysis of a specimen of Cheshire galls made by *Watson Smith* in 1869 gave the following results:—Tannin, 26·71; gallic acid, trace; woody fibre, 47·88; moisture, 20·61; and colouring matter and loss, 4·80 per cent.

Specimens of old oak-apple galls collected by us during the winter in Surrey contained only 11 per cent. of tannin as estimated by *Procter's* hide-powder method, but, when examined by a colorimetric method, the amount of gallic and tannic acids, in terms of gallotannic acid, was 30·7 per cent.

Fig. 27.—Gall of *C. Kollari.*

These galls yielded a good ink, and there seems to be no reason why British galls collected at the right period should not be used in admixture with the richer foreign varieties by ink manufacturers.

The writer is indebted to Mr. *R. M. Prideaux* for the specimens of oak marbles, the analyses of which are given in the subjoined table, which also includes, for comparison, the analysis of a rose-gall (bedeguar) which contained a large number of larvæ (*Rhodites rosæ*). All these galls were produced in the season of 1922, and are, therefore, typical of different stages of growth. The tannin and gallic acid were estimated by the colorimetric method.*

THE COMPOSITION OF BRITISH GALLS.

(*Factor* = 2·1.)

	Moisture. Per cent.	Soluble extract. Per cent.	Tannin. Per cent.	Gallic acid. Per cent.
1. Black gall, . .	35·66	6·00	3·25	..
2. Yellow, empty, . .	14·70	19·00	12·93	1·25
3. Pale brown, . .	18·93	62·0	36·74	1·50
4. Blind gall, brown, .	17·78	31·25	28·25	0·93
5. Rose gall, . .	..	..	19·74	0·0

* *Analyst*, 1923, xlviii., 12.

No. 1 had a white, spongy interior; it contained no larva in the centre, but had eight or ten small larvæ round the periphery (see Fig. 15).

No. 2 was a pierced gall, and contained a good deal of dust.

No. 3 had a large larva in the central cavity.

No. 4 was a blind gall without a central chamber, though it had one small larva on the exterior just below the epidermis.

It is interesting to note that the gall containing the living larva in the centre chamber was the richest in tannin, and that this fact supports the general practice of collecting Aleppo galls at a period shortly before the larva reaches maturity.

A comparison of these results strongly suggests that the true larvæ (of *Cynips Kollari*) produce tannin as an excretory product, whereas the inquiline larvæ (as typified by No. 1) are unable to effect this decomposition.

The *French galls* sometimes met with in commerce are slightly larger than ordinary oak-marbles, which they closely resemble in general appearance. They are formed upon the shoots of *Quercus ilex* in Mediterranean districts. Probably some of the varieties of Punjab galls are obtained from this species of oak.

OTHER VARIETIES OF GALLS.—There are numerous other kinds of galls, some of which are of considerable importance as tanning materials, but they do not appear to have been used in the manufacture of ink, though probably some of them would be suitable for the purpose.

The *small-crowned Aleppo galls*, which are occasionally found mixed with ordinary Aleppo galls, are also produced upon *Quercus infectoria*, but by a different insect (*C. polycera*). They are about the size of a pea, and have a circlet of small projections at the top.

Pistachio galls are produced by *Anopleura lentisci* on plants of the *Pistachio* order, and are exported from Bokhara together with pistachios. They are red galls, about the size of a cherry, and have a characteristic taste.

Mecca or *Bassorah galls* are produced upon an oak by *Cynips insana*. A sample analysed by *Bley*,* had the following composition:—Tannic acid, 26·00; gallic acid, 1·60; fatty oil, 0·60; resin, 3·40; extractives and salts, 2·00; starch, 8·40; woody fibre, 46·00; and moisture, 12 per cent.

Tamarix galls, also known as *red galls*, are formed on *Tamarix orientalis* and other plants of the same order. They are of a bright red colour, and are about 1 cm. long by 0·5 cm. broad. They are extensively employed in dyeing and tanning, and in India they are

* *Archiv. Phram.*, 1853, lxxv. (2), 138.

used medicinally by the natives. Similar galls are produced on *T. articulata* in Morocco.

The galls formed on the American "live oak," *Q. virens*, are stated to contain 40 per cent. of tannic acid, and are very similar to Aleppo galls. A soft, spongy, and very astringent gall is formed on the Californian oak, *Q. lobata.**

Terebinth galls are due to the action of aphides on certain species of *Terebinthaceæ* growing in the countries bordering on the Mediterranean. They are red in colour, long and flat, and have horn-shaped projections. Within them is a large cavity in which fragments of

FIG. 28.—Gall wasp (*Cynips Kollari*). × 5½.

the aphides can usually be discerned. They contain a considerable amount of tannin and a resinous juice which readily exudes. These galls are sometimes termed *apples* or *galls of Sodom*.

Watt † states that the galls produced upon *Pistachi terebinthus* in India are regarded by the natives as valueless, though the leaves are used for dyeing and tanning. They are sold in Bombay as *pistachio galls* (*vide supra*).

* Trimble, *The Tannins*, vol. i., p. 63. † *Dict. of Economic Products.*

Tannins.

The substances to which the general name "tannin" has been applied are compounds possessing certain chemical and physical characteristics in common. They are widely distributed throughout the vegetable kingdom, and it is not improbable that many of them are individual substances, just as are the different fatty acids which occur in vegetable oils.

When separated in a state of purity or approximate purity, tannins are odourless white or brown substances, with a very astringent taste. They are insoluble in chloroform and carbon disulphide, but dissolve in water, alcohol, and ether. They yield blue or green insoluble compounds with iron salts, and most of them are precipitated by potassium chromate. They also usually combine with antimony, with lead, and many other metals to form soluble salts. With lime water they yield precipitates of varying colour, and with gelatin they form an insoluble compound, as in the formation of leather.

Tannins are oxidised by nitric acid and by potassium permanganate, the latter reaction forming the basis of a quantitative method of determination.

CLASSIFICATION OF TANNINS.—Tannins are frequently described as "iron-blueing" or "iron-greening," according to the colour of the precipitate they form with iron salts. This difference is evidently one of the constitution, for, as *Stenhouse* * first showed, the members of one group of tannins can be converted into gallic acid and yield pyrogallol, whilst those of the other group do not give these reactions.

Thus, when heated to 160° C., different products of decomposition are formed, the "iron-blueing" tannins, of which gallotannin may be taken as the type, yielding metagallic acid and pyrogallol, whilst the "iron-greening" tannins produce metagallic acid and catechol.

Thorpe's method of preparing pyrogallol by heating gallotannic acid in glycerin has been used as a qualitative test of the nature of the tannin: 1 grm. of the tannin is slowly heated to 160° C. in 5 c.c. of glycerin, and the temperature then raised to 200-210° C. for 20 minutes. The liquid is next diluted with 10 c.c. of water and extracted with an equal volume of ether (or extracted with ether without previous dilution, *Trimble*), and the residue from the ethereal extract dissolved in water and tested for pyrogallol or catechol by the following tests :— †

* *Mem. Chem. Soc.*, 1842, i., 133.

† Trimble, *The Tannins*, i., p. 26.

Reagent.	Pyrogallol. 1 per cent. solution.	Catechol. 1 per cent. solution.
Ferric chloride . .	Red, turning brown.	Green colour.
Ferric acetate . .	Dark purple.	,, ,,
Lime water . .	Purple, then brown.	Clear red.
Pinewood moistened with hydrochloric acid . . .	No change.	Violet colour.
Melting-point .	131° C.	111° C.

Mitchell's reagent (a solution of 0·1 gramme of ferrous sulphate and 0·5 gramme of Rochelle salt in 100 c.c. of water) affords a rapid means of distinguishing between the two classes of tannins, one of which gives violet-red or violet-blue colorations, and the other a dirty green coloration in neutral solution, and a violet coloration in acid solution.*

The *Goldbeater's Skin Test.*—A test for tannins has been based by Atkinson and Hazelton † on their fixation on goldbeater's skin, which is subsequently stained with ferric chloride. This test has been shown by Price ‡ to be capable of detecting 0·005 per cent. of gallotannin. The fragment of skin is pinned to a flat surface of paraffin wax in a watch-glass, and treated for 10 minutes with 1 c.c. of 2 per cent. hydrochloric acid, and afterwards washed with distilled water for 2 minutes at a constant drip of 2 drops per second. It is next treated for 30 minutes with 1 c.c. of the solution to be tested for tannins, and washed as before, for 15 minutes. Finally, 1 c.c. of a 1 per cent. solution of ferrous sulphate or ferric chloride is left standing on the skin for 15 minutes, and the skin then washed for 2 minutes. When dry, the skin may be mounted for comparison with skins treated with gallotannin solutions of known concentration.

Both forms of tannin react with osmic acid, to form red-violet to black-violet compounds (Mitchell).

When boiled with alkalis the "iron-greening" tannins yield protocatechuic acid and phloroglucinol or acetic acid, whilst the "iron-blueing" tannins are converted into gallic and ellagic acids.

The elementary composition of the different tannins has been suggested by *Trimble* § as a possible means of classification. Thus, the gall tannins, or "iron-blueing" group, contain about 52 per cent. of carbon and about 3·5 per cent. of hydrogen, whilst the

* *Analyst*, 1923, xlviii., 2.

† *Biochem Journ.*, 1922, xvi., 516.

‡ *Analyst*, 1924, xlix., 25.

§ *Loc. cit.*, ii., p. 132.

"iron-greening" tannins have 60 per cent. of carbon and 5 per cent. of hydrogen—*e.g.* :—

Group I.

	Carbon. Per cent.	Hydrogen. Per cent.
Gallotannin, ...	52.10	3.52
Chestnut wood tannin	52.11	4.40
Chestnut bark tannin	52.42	4.67
Chestnut tannin (*Nass*)	52.07	3.97
Sumach tannin (*Löwe*)	52.42	3.56

Group II.

	Carbon. Per cent.	Hydrogen. Per cent.
Oak-bark tannin (av. of 9) . . .	59.79	5.08
Kino tannin (*Bergholz*) . . .	59.65	4.87
Oak-bark tannin (*Etti*)	59.25	4.99
Catechu tannin (*Löwe*)	61.93	4.80
Tormentilla tannin (*Rembold*) . .	60.75	4.65

The tannins in Group I. give a white precipitate, changing to blue with lime water, whilst in the case of the tannins in Group II. the colour of the precipitate is light pink, changing to red or brown. Bromine water precipitates the tannins in the second group, but not those of the first group.

The differences in the composition of tannins from different sources were also shown in analyses made by Koerner and Petermann.*

Tannin from	Carbon. Per cent.	Hydrogen. Per cent.
Quebracho	63.79	4.81
Oak-wood	53.05	4.81
Chestnut-wood	51.28	4.40
Mimosa bark	57.37	5.57

* *Chem. Zeit.*, 1904, xxviii., Rep. 328.

Bennett * has described tests for distinguishing between valonia, oak-wood and chestnut tannins. Valonia tannin yields a dense yellow crystalline precipitate ($C_6H_2Br_3O.Br$) on adding bromine water to the solution of the product of its dry distillation. Chestnut tannin treated in the same way gives no precipitate, whilst oakwood tannin gives a small amount of a dark product melting at 107° to 112° C.

SUITABILITY OF TANNINS FOR INK-MAKING.—Only the "iron-blueing" tannins are suitable substances for the manufecture of black ink, as has been shown by *Schluttig* and *Neumann*,† who found that mixtures of extracts of pine, catechu, quebracho, kino, and hemlock with solutions of iron salts gave bright green colorations on paper, but that after six months' exposure only rust-like stains were left.

Notwithstanding these drawbacks, however, it is stated by *Lehner* ‡ that yellow catechu extract and kino extract are used in Austria as raw materials for ink.

Good black inks can be prepared from algarobilla, divi-divi, myrobalans, valonia, and sumach, all of which contain "iron-blueing" tannins.

Oak-bark tannin, although an "iron-greening" tannin, also contains a substance giving a blue precipitate with iron salts, and can, therefore, be used in the manufacture of ink (*vide infra*).

The most important of the tannins suitable for ink are described individually in the following pages.

Chestnut Bark and Wood.

The Spanish or Sweet Chestnut (*Castanea vesca*) is a large tree, frequently 80 feet or more in height, which grows abundantly in the countries surrounding the Mediterranean, and in sheltered districts as far north as Scotland. In America it is common in many of the States as far west as Indiana. The fruit is the well-known chestnut, which is largely imported into this country.

CHESTNUT EXTRACT.—An aqueous extract of chestnut wood or bark is prepared extensively in Pennsylvania and Virginia, the decoctions being subsequently evaporated to a solid mass. According to *Trimble*,§ it is impossible to manufacture a good extract without the use of a vacuum pan. It is said to be frequently adulterated

* *Journ. Soc. Chem. Ind.*, 1914, xxxiii., 1186.
† *Die Eisengallustinten*, p. 38.
‡ *Die Tinten-Fabrikation*, 1922, p. 26.
§ *The Tannins*, ii., p. 129.

with molasses or glucose, and is itself employed to adulterate oak bark extract.

CHESTNUT TANNIN.—*Sheldon,** who appears to have been the first to call attention to the value of chestnut wood as a tanning and dyeing material, asserted that it contained twice as much tannin as oak bark.

Trimble (*loc. cit.*) found air-dried chips to contain 7·85 per cent. of tannin, which is slightly higher than the amount found by *Sheldon*; and *Simand* † found 8·5 per cent. in chestnut wood, and 23·52 per cent. in chestnut-wood extract of 31° Bé., the determinations being made by *Löwenthal's* permanganate method.

Nass ‡ was the first to prepare a tannin from chestnut wood, and to determine its composition and properties. The aqueous extract of the wood was fractionally precipitated with sodium chloride, and the final fractions dialysed and then extracted with ethyl acetate.

In this way he obtained a white preparation which was soluble in water, alcohol, ether, and glycerin, and gave the following reactions when tested in a 1 per cent. solution.

Reagents.	Chestnut tannin.	Gallotannic acid.
Ferrous salt	No change.	No change.
Ferric ammonium sulphate	Blue-black precipitate.	Blue-black precipitate.
Tartar emetic + ammonium chloride	Slight precipitate.	Slight precipitate.
Bromine water	No precipitate.	No precipitate.
Lime water	Light precipitate, becoming light blue.	White precipitate, becoming light blue.
Sulphuric acid (1 : 9)	No deposit on boiling.	No deposit on boiling.

When heated to 200° C. it was converted into pyrogallol and metagallic acid, and gave an acetyl derivative closely resembling that of gallotannic acid.

Its elementary composition was also found to be very similar to that of gallotannin, as is shown by the following results obtained by *Nass* and by *Trimble* § :—

* *Amer. Journ. Science,* 1819, i., 313.
† *Dingler's polyt. Journ.*, 1885, cclv., 487.
‡ *Zeit. anal. Chem.*, 1886, xxv., 134; also Trimble, *The Tannins*, ii., p. 124.
§ *Loc. cit.*, p. 127.

	Chestnut tannin (*Nass*). Per cent.	Chestnut wood tannin (*Trimble*). Per cent.	Chestnut bark tannin (*Trimble*). Per cent.	Gallotannic acid. Per cent.
Carbon . .	52.20	52.42	52.11	52.17
Hydrogen .	3.97	4.67	4.40	3.10

In *Trimble's* opinion this similarity in composition and reactions renders it highly probable that chestnut tannin is identical with the gallotannic acid from galls.

INK FROM CHESTNUT WOOD.—*Sheldon* (*loc. cit.*) in 1819 found that chestnut wood contained $\frac{6}{7}$ as much substance giving a black coloration with iron (*i.e.*, tannin), as was present in logwood (hæmatoxylin). He stated that it was probably unequalled as a material for ink, since it gave a rich blue-black colour with iron, whilst galls or sumach used in the same proportion had a redder shade. The ink formed by chestnut decoction was blue, but after drying on paper it yielded an intense black. The permanence of the ink was tested by exposing the writing to the sun and air, and was found highly satisfactory.

Schluttig and *Neumann*,* however, in their comparative tests on the stability of inks prepared from different tannin materials, found that chestnut iron-ink, originally blue-black, was fainter than the ink from most of the other "iron-blueing" tannins (p. 56).

In 1825 *Giroud* took out a patent (Eng. Pat. No. 5285) for a substitute for galls, to which he gave the name of "damajavag." This was prepared by soaking 1 cwt. of the wood of the chestnut tree, or shells of the nuts, with water for twelve hours, and then boiling it with 180 to 200 quarts of water and evaporating the decoction to a paste, which was to be used in the manufacture of ink, or in tanning.

An ink prepared by the writer from chestnut extract had a good blue-black colour. On standing exposed to the air for a month it yielded a deposit containing 7·37 per cent. of iron.

SUMACH.

Sumach or *Sumac* is the name given to the leaves of various plants belonging to the natural order *Rhus*.

* *Loc. cit.*, p. 38.

Of these, the Silician sumach, *Rhus coriaria*, grows wild in Spain, Portugal, and other Mediterranean districts, and is also widely cultivated in these countries. The most esteemed variety of Sicilian sumach, known as *Alcamo*, occurs in commerce as a light green

FIG. 29.—Sumach (*Coriaria myrtifolia*).

powder, with an aromatic odour. A second and inferior variety, which is chiefly used in dyeing, has a more yellow shade and contains less tannin.

The best French sumach is very similar to that grown in Sicily.

Another French variety, known as *redou*, is obtained from *Coriaria myrtifolia* (Fig. 29).

In preparing sumach for the market, the branches are dried in the sun, and the leaves removed and ground to powder in mills.

The leaves of the Venetian sumach, *Rhus cotinus*, a shrub cultivated in Italy and the south of France, contains a yellow dyestuff, and a tannin which gives an olive-green compound with iron salts, and is therefore unsuitable for ink-making.

In America two species of *Rhus*, *R. copallina* and *R. glabra*, both of which contain much less tannin than Sicilian sumach, are extensively used as tanning materials.

SUMACH TANNIN.—The proportion of tannin in sumach varies considerably, but the usual limits are from about 13 to 20 per cent.

Stenhouse * was the first to show the similarity in composition and properties between the tannin of sumach and gallotannic acid, both yielding gallic acid and pyrogallol. The percentage composition of his sumach tannin was: Carbon, 49·73 to 50·12; hydrogen, 3·64 to 3·76; and oxygen, 46·24 to 46·51.

Löwe † obtained a purer product by extracting Sicilian sumach with alcohol, treating the residue from the extract with water, extracting the tannin by means of acetic acid, and purifying it by repeatedly dissolving it in water, and precipating it with sodium chloride. Gallic acid (which was not identified) would be left in solution in the sodium chloride treatment.

Löwe confirmed *Stenhouse's* statement as to the formation of gallic acid from the tannin. Crystals of the former were obtained by heating the tannin solution either alone or with 2 per cent. of sulphuric acid for several hours in a sealed tube placed in a brine bath.

The properties of the Sicilian sumach tannin were found to be identical with those of gallotannin, and analysis showed them to have the same composition, corresponding with the formula $C_{14}H_{10}O_9$.

Löwe was doubtful whether the tannin of other species of sumach could also be regarded as identical with gallotannin. Thus a tannin prepared from Tyrol sumach contained 52·3 per cent. of carbon and 3·8 per cent. of hydrogen, corresponding with the formula $C_{16}H_{14}O_{10}$. Moreover, this tannin differed from that of Sicilian sumach in not yielding gallic acid when heated in a sealed tube with sulphuric acid.

Sumach contains a small quantity of a yellow dyestuff, *quercetrin*.

INK FROM SUMACH.—As the tannin of sumach is identical, or at least allied to that of galls, it was to be anticipated that it would yield an ink of a very similar character, only modified slightly by

* *Mem. Chem. Soc.*, 1842, i., 135. † *Zeit. anal. Chem.*, 1873, xii., 128.

the colouring matter of the leaves. In fact, *Ribeaucourt* * found that the ink made from it had a greenish shade.

Lewis,† who made experiments in 1763 with sumach as an ink material, came to the conclusion that it was inferior to galls as a source of tannin.

Schluttig and *Neumann*,‡ however, have shown that sumach iron-ink is but little inferior in durability to ink prepared from Chinese galls, and superior to "Knoppern" ink. According to *Viedt*,§ ink is occasionally prepared from sumach on a manufacturing scale.

Divi-divi.

Divi-divi is the name given in commerce to the dried pods of the South American shrub, *Cæsalpinia coriaria* (Fig. 30), which was not

Fig. 30.—Divi-divi pods.

known in Europe until the latter half of the eighteenth century. It grows in low-lying marshy lands, attaining a height of twenty to thirty feet.

The pods are of a dark brown colour, and about one and a half to three inches in length. They have a very astringent taste, due to the tannin, which is for the most part concentrated in the rind immediately beneath the epidermis. The recorded amount of tannin

* *Ann. de Chim.*, 1792, xv., 156.
† *Loc. cit.*, p. 382.
‡ *Loc. cit.*, p. 38.
§ *Dingler's polyt. Journ.*, 1875, ccxvi., 453.

ranges from 30 to 52 per cent. A commercial sample examined by Mitchell's colorimetric method contained 36 per cent.

A representative analysis of the pods is:—Water, 13·5; tannin, 41·5; non-tannin substances, 18; ash, 1·6; and insoluble matter, 25·4 per cent.*

At Porlamar and La Guaira the tannin is extracted from the pods by a patent process and the extract compressed into tablets. These are stated to contain up to 80 per cent. of tannin and about 16 per cent. of tannin glucose.

DIVI-DIVI TANNIN.—*Stenhouse* † separated a tannin from divi-divi, which he found to have the following composition:—Carbon, 50·12; hydrogen, 3·72; and oxygen, 4·62.

This tannin yielded gallic acid and pyrogallol, and formed deep blue insoluble compounds with ferric salts, and was thus very similar in composition and properties to gallotannic acid.

In a more extended research, *Löwe* ‡ found that the tannin of divi-divi behaved with most reagents like gallotannic acid, from which it was distinguished, however, by yielding a deposit of ellagic acid when heated in aqueous solution in a sealed tube.

He therefore described this tannin as ellagitannic acid, and ascribed it to the formula $C_{14}H_{10}O_{10}$, which may be regarded as gallic acid, $C_{14}H_{12}O_{10}$, minus 2 atoms of hydrogen, or gallotannin, $C_{14}H_{10}O_9$, plus 1 atom of oxygen.

Löwe also found the same tannin in myrobalans.

A specimen of divi-divi examined by the writer contained 34 per cent. of tannin estimated colorimetrically, and expressed in terms of gallotannic acid.

Another sample gave the following results, in which the gallic acid colorimetric equivalent was multiplied by the empirical factor 2 to obtain the tannin.§

Moisture. Per cent.	Total extract. Per cent.	Tannin. Per cent.	Gallic acid. Per cent.	Total Pyrogallol equivalent. Per cent.
11·49	74·0	32·8	2·6	12·66

INK FROM DIVI-DIVI.—*Stenhouse* (*loc. cit.*) states that calico printers had attempted to use divi-divi as a substitute for galls, but had not found it satisfactory, owing to the large proportion of other extractive matters (gums).

In the case of ink this would not be so objectionable, and in fact

* Hoar, *Commerce Reports*, July, 1923.
† *Mem. Chem. Soc.*, 1842, i., 141.
‡ *Zeit. anal. Chem.*, 1875, xiv., 35.
§ *Analyst*, 1923, xlviii., 14.

Viedt * asserts that divi-divi is sometimes used in Germany as a source of ink-tannin.

An ink was prepared by the writer from an extract of divi-divi (5 grms.), treated with 1 grm. of ferrous sulphate. The deposits yielded by this ink contained from 6·77 to 7·77 per cent. of iron.

FIG. 31.—Myrobalans.

MYROBALANS.

The dried fruit of different species of *Terminalia* growing in India and the East Indies is sold as a tanning and dyeing material under the name of myrobalans (Fig. 31).

The ripe fruit weighs between 5 and 10 grms., and has a very astringent taste, due to the tannin in the husk.

The Indian species, *T. chebula*, which yields the "black" or "chebulic" myrobalans of commerce, is extensively used in conjunction with iron salts as a black dye, and is also employed in the manufacture of ink.

The earliest mention of the possible use of myrobalans as a substitute for galls is that made by *A. Johnson* † in a communication to the Society of Arts in 1801, in which he stated that the natives in India used them to give a black colour to leather, mixing the powder with iron filings and water.

A committee of the Society appointed to report on the subject found that the pulp and outer husk of the fruit gave a rich black colour with ferrous sulphate.

Sometimes a small proportion of myrobalans is mixed with galls for the preparation of writing inks, but they are mainly used as a raw material for copying inks, for which purpose their high proportion of gums renders them particularly suitable. It is well known that roasting improves myrobalans for ink-making, but the changes brought about by the process have not hitherto been ascertained.

Ink prepared by the writer from myrobalans was of a good blue black colour, and yielded insoluble deposits containing about 6 per cent. of iron.

* *Dingler's polyt. Journ.*, 1875, ccxvi., 453. † *Trans. Soc. Arts.*, 1801, xix., 343.

THE TANNIN OF MYROBALANS.—*Löwe* * found about 1 per cent. of gallic acid in myrobalans, and extracted a tannin which contained 49·42 per cent. of carbon and 3·16 per cent. of hydrogen, corresponding with the formula $C_{14}H_{10}O_{10}$.

When heated in a sealed tube at 108°-110° C., a solution of this tannin yielded a deposit of ellagic acid; and from this fact and the elementary analysis, *Löwe* concluded that it was ellagitannic acid, identical with that of divi-divi.

Zölffel † confirmed *Löwe's* statement of the occurrence of 1 per cent. of gallic acid, but found that the tannin was a mixture of ellagitannic acid, and a glucoside of gallotannic acid, the former being in the greater proportion.

Freudenberg and *Fick* ‡ state that chebulinic acid, the tannin of myrobalans, is a crystalline compound of digalloyl glucose with a dibasic phenolic acid, $C_{14}H_{14}O_{11}$, which loses two molecules of water in the process of combining. This phenolic acid yields pyrogallol when distilled under reduced pressure, and we may therefore assume that it contains a pyrogallic group. A second pyrogallic group is present in the digalloyl group, as shown in the formula:

$$[C_6H_2(OH)_3 . CO . O . C_6H_2(OH)_2 . CO] . C_6H_{11}O_6 + C_{14}H_{14}O_{11} - 2H_2O.$$

The molecular weight of this compound, $C_{34}H_{30}O_{23}$, is 806, which agrees fairly well with the results experimentally obtained, and the colorimetric ratio between two pyrogallic groups and the tannin is therefore as 1 : 3·22, or, in terms of gallic acid, as 1 : 2·14, which is practically the same as in the case of gallotannin from Chinese galls. This factor was accordingly used in the following analyses of myrobalans recently made by the writer. §

COMPOSITION OF MYROBALANS.
(*Factor* = 2·16.)

	Moisture. Per cent.	Extract. Per cent.	Tannin. Per cent.	Gallic acid. Per cent.	Total pyrogallol equivalent Per cent.
Raw, . .	7·25	32·8 (6 days) 33·0 (14 ,,)	21·6	2·8	8·53
Roasted (*a*), .	9·70	49·6	34·5	7·2	15·40
,, (*b*), .	. .	50·8	33·4	7·5	15·33
Commercial myrobalans liquor.	97·08	2·92	1·62	0·5	0·87

* *Zeit. anal. Chem.*, 1875, xiv., 35.
† *Arch. der Pharm.*, 1891, ccxxix., 155.
‡ *Ber.*, 1918, lii., 1238; 1920, liii., 1728.
§ *Analyst*, 1923, xlviii., 14.

As a rule, roasted myrobalans do not yield a much higher extract than the raw product, but, in the case of this sample, the roasting process had caused not only the pericarp, but also the kernel, to become dark brown and friable.

Valonia.

Valonia is the commercial name for the acorn cups of certain species of oaks growing in Asia Minor and different parts of Greece, of which the most important are *Q. œgilops* and *Q. macrolepsis*.

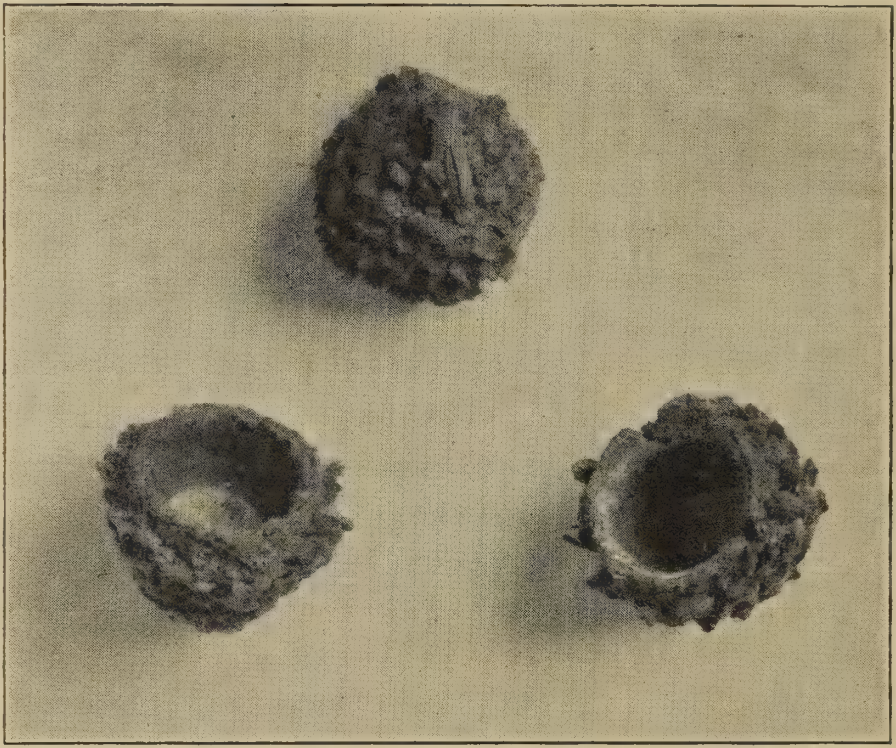


Fig. 32.—Valonia.

The best sorts are gathered before the fruit is quite ripe in April, those beaten from the trees in September and October being poorer in tannin.

The cups (containing the acorns) are first partially dried on the ground and then conveyed by mules to Smyrna, where they are stored in warehouses until slight fermentation sets in and causes the acorns to fall from the cups.

If exposed to rain after gathering, the acorn cups turn black and lose a considerable amount of tannin by fermentation.

As met with in commerce, valonia consists of semi-circular prickly backed cups, about 50 mm. in diameter (see Fig. 32).

The amount of tannin they contain varies greatly with the district, species of oak and time of collection, but usually ranges from about 20 to 45 per cent.

The following percentages have been recorded *inter alia*: 32·4 (*Handtke*); 38 (*Gallow*); 22·6 to 39·2 (*Rothe*); and 31·6 to 35·64 (*Simand*).

Eitner * examined eighteen samples of different origin of the harvest of 1886, and found them to yield from 42·4 to 51·9 per cent. of total extract, 1·6 to 3 per cent. of soluble ash, and 21·28 to 30·2 per cent of tannin.

The best valonia is that obtained from Smyrna, the Greek and Albanian products being held in much smaller esteem.

In 1852 the prices per cwt. were as follows:—Smyrna, 14*s.* to 15*s.*; Morea, 10*s.* to 12*s.*; and Camata, 14*s.* to 16*s.* (*Tomlinson*). The prices given by *Procter* in 1885 were considerably higher, viz., Smyrna, 12*s.* 6*d.* to 20*s.* 6*d.*; Morea, 10*s.* 6*d.* to 18*s.* 6*d.*; and Camata, 15*s.* to 19*s.* per cwt.

THE TANNIN OF VALONIA.—This appears to be mainly ellagitannic acid, judging by the results of *Böttinger*,† who extracted the tannins from valonia, divi-divi, and algarobilla, and prepared the acetyl derivative of each. The proportion of acetyl in the valonia tannin (44·1 per cent.) was nearly the same as that of divi-divi (43·19 per cent.) and algarobilla (43·9 per cent.), and hence *Böttinger* concluded that the preparations were identical in composition.

The following results were recently obtained by the writer in the analysis of a commercial sample of valonia:— ‡

Moisture. Per cent.	Total extract. Per cent.	Tannin. Per cent.	Gallic Acid. Per cent.	Total Pyrogallol equivalent. Per cent.
13·13	49·0	46·0	3·0	17·3

Another sample contained 37·5 per cent. of gallotannin and gallic acid, estimated together by Mitchell's colorimetric method, whilst the amount found by Procter's hide-powder method was only 20·0 per cent.

The filtrate from the hide powder contained iron-colouring substances (gallic acid), corresponding to 2·5 per cent. of gallotannic acid.

* *Der Gerber*, 1887, xiii., 18.

† *Ber.*, 1884, xvii., 1503.

‡ *Analyst*, 1923, xlviii., 14.

Ink from Valonia.—Valonia yields a very rich bluish-black ink, and appears to be a very suitable raw material for the manufacture, especially if used in admixture with Chinese galls.

The deposits yielded by the ink on exposure to the air are very similar to those given by gall or divi-divi inks. Thus the deposits from experimental inks contained from 11·5 to 12·8 per cent. of iron oxide.

Oak-Bark Tannins.

Owing to the fact that infusions of oak bark give a blue coloration with iron salts, the tannins present were formerly regarded as identical with gallotannic acid. This error was first pointed out by *Stenhouse*,* who showed that an infusion of oak bark differed from a solution of gallotannic acid in not yielding gallic acid or pyrogallol.

In 1867 *Grobowski* found that, instead of gallic acid, an amorphous red compound, "oak red," was produced, which *Etti* † obtained by boiling an oak tannin with dilute sulphuric acid, and concluded to be an anhydride with the formula

$$2C_{17}H_6O_9 - H_2O = C_{34}H_{26}O_5.$$

An extended series of researches on the oak tannins were then made independently by *Etti*, by *Löwe*, and by *Böttinger*, but the most conflicting results were obtained. Thus *Etti* prepared an oak tannin which did not dissolve in water and gave a green coloration with ferric salts, whilst *Löwe* obtained soluble tannins with the formulæ $C_{28}H_{28}O_{14}$ and $C_{28}H_{30}O_{15}$, which gave blue precipitates with iron solutions.

Trimble ‡ has given an excellent summary of these different results, though without succeeding in reconciling them. He himself has made numerous preparations, and has found the average composition of nine of these to be as follows:—Carbon, 59·79; hydrogen, 5·08; and oxygen, 35·13 per cent.—results which correspond best with the formula of *Etti's* tannin, $C_{20}H_{20}O_9$.

In *Trimble's* opinion there is no question that oak tannins give green colorations with iron salts, and he attributes the blue colorations given by oak-bark infusions to the presence of an associated colouring matter. In the case of the chestnut oak he separated this "iron-blueing" compound by first precipitating the oak tannins with basic lead acetate.

* *Mem. Chem. Soc.*, 1842, i., 140.
† *Monatsh. f. Chem.*, 1880, i., 262.
‡ *The Tannins*, ii., 90.

REACTIONS OF OAK TANNINS.—On heating oak-bark tannins to 190° C. catechol is formed as the main decomposition product, whilst on fusion with caustic alkali protocatechuic acid is obtained.

The colour reactions vary greatly with the species of oak whence the tannins were derived, which is evidence that they are not identical.

Trimble * gives the following table of the reactions of the tannins separated from two species of oak bark compared with those given by gallotannic acid :—

Reagent.	English oak, *Q. robur.*	Indian oak, *Q. sessiliflora.*	Gallotannic acid.
Copper sulphate.	Precipitate.	—	No precipitate.
Copper sulphate + ammonia.	Red brown precipitate.	—	Brown precipitate.
Stannous chloride and HCl.	Violet colour.	Violet colour.	Slight green colour.
Sodium sulphite.	Pink colour.	Yellow colour.	Slight pink colour.
Bromine water.	Yellow precipitate.	Yellow precipitate.	No precipitate.
Ferric chloride.	Blue green colour and green precipitate.	Green colour and precipitate.	Blue colour and precipitate.
Ferric chloride + ammonia.	Purple brown precipitate.	Purple brown precipitate.	Purple precipitate.
Ferric ammonium sulphate.	Blue green colour and green precipitate.	Green colour and precipitate.	Blue colour and precipitate.
Lime water.	Precipitate turning pink.	Precipitate turning pink.	Precipitate turning blue.

AMOUNT OF TANNINS IN OAK BARK.—*Procter* gives the proportion of tannins in European oak bark as 10 to 12 per cent., and *Trimble* † found the bark of different species of American oaks to contain from 4·04 to 14·21 per cent., whilst an English oak bark gave 12·37 per cent. calculated on the dry substance.

The chief species of oak from which the commercial bark is derived are *Q. pedunculata*, *sessiliflora*, and *rubescens*, the first of which usually contains more tannin than the others.

Eitner ‡ has shown that the amount of tannin varies with the

* *Loc. cit.*, ii., 48.
† *Ibid.*
‡ *Der Gerber*, iv., 85.

season. Thus in the case of the bark from *Q. pedunculata* he obtained the following results :—April, 14·80 ; May, 10·71 ; June, 12·33 ; July, 9·8 ; and August, 11·23 per cent.

Weiss * analysed commercial oak barks of different origin with the following results :—

Origin.	Tannin. Per cent.	Ash. Per cent.
Hungarian (3) . .	10.36 – 13.47	5.68 – 7.31
German (3) . .	11.87 – 16.18	6.27 – 8.52
French (3) . . .	13.82 – 16.22	6.14 – 7.77
Danish (3) . . .	13.86 – 16.22	6.66 – 7.81
Swedish . . .	12.02 – 14.59	5.55 – 7.05
Average . . .	13.50	6.82

INK FROM OAK BARK.—*Stenhouse* (*loc. cit.*) found that a good blue-black ink could be prepared from an infusion of oak bark, in which respect it differed from the infusions of kino, larch, and alder barks, which only gave green colorations with iron salts.

According to *Prechtl*,† oak bark was used fifty years ago, in conjunction with other substances, in the manufacture of ink. Thus he gives the following formula for the preparation of ink from oak-bark galls and *Knoppern* :—Galls 9 lbs., logwood 1½ lbs., rasped oak bark 8 lbs., Knoppern 6 lbs., gum 2 lbs., ammonium chloride ½ lb., infused in 40 quarts of water and 24 quarts of vinegar, and the infusion mixed with ferrous sulphate.

Since the pure oak tannins are "iron-greening" substances, whilst the blue-black colour given by oak-bark infusions with iron salts is only due to the presence of an associated substance (*vide supra*), the use of oak bark for ink is not economical. Moreover, ink prepared exclusively from the infusion has been shown by *Schluttig* and *Neumann* ‡ to be somewhat less stable on exposure to light and air than the inks from galls, divi-divi, or other substances containing only "iron-blueing" tannins.

Lehner, however, recommends the use of spent tan bark for the preparation of a cheap ink.§

* *Der Gerber*, 1885, ii., 181.
† *Technol. Encyclop.*, 1852, xviii., 460.
‡ *Die Eisengallustinten*, p. 38.
§ *Die Tinten-Fabrikation*, 1922, p. 21

Gallotannic Acid or Gallotannin.

The tannin which is best known is that contained in galls, and to this name of *gallotannic acid* has been given to distinguish it from *quercitannic acid* and other tannins. It is present in Aleppo, Chinese and Japanese galls, and in *Knoppern*, and a closely allied tannin has been found in sumach, myrobalans, and algarobilla.

Pelouze * prepared gallotannic acid by extracting powdered galls with ether containing water, and showed that on exposure to the air in an aqueous solution it gradually yields an insoluble deposit consisting mainly of gallic acid.

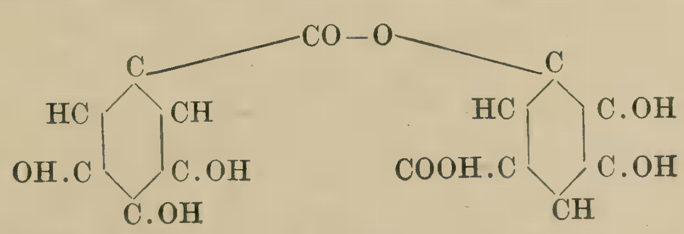
Strecker † came to the conclusion that gallotannic acid was a glucoside, which was decomposed on fermentation, in accordance with the equation

$$\underset{\text{Glucoside.}}{C_{34}H_{28}O_{22}} = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Tannic acid.}}{2C_{14}H_{10}O_9} - H_2O.$$

Subsequently it was stated by *Schiff* ‡ that perfectly pure gallotannic acid was free from dextrose, and was an anhydride containing two gallic acid groups—*i.e.*, digallic anhydride. In his opinion, the dextrose in *Strecker's* preparation was originally present in the galls, and had been extracted simultaneously with the tannic acid.

Trimble § concludes that, although gallotannic acid can be so purified as to be eventually only digallic anhydride, it is rarely, if ever, met with in that state in the "pure" article of commerce, which contains variable amounts of dextrose in a loose state of combination. In his opinion the commercial article must be regarded either as a glucoside of digallic acid, or as a mixture of the glucoside and of the pure anhydride.

The following constitutional formula represents Schiff's view of the formation of a digallic acid by the condensation of two molecules of gallic acid, with the loss of one molecule of water :—

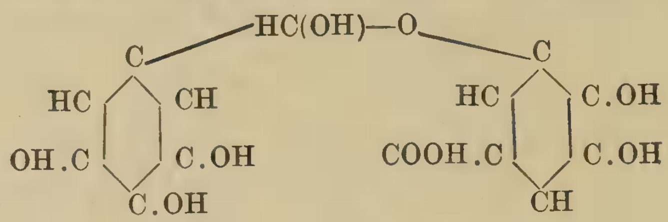


This long-accepted formula is not in keeping with the fact that gallotannin has been shown by the boiling-point method to have a molecular weight of over 600. Moreover, in this old formula,

* *Ann. Chem. Pharm.*, 1833, liv., 337.
† *Ann. Chem. Pharm.*, 1854, xc., 238.
‡ *Ibid.*, 1873, clxii., 43.
§ *The Tannins*, i., p. 29.

$C_6H_2(OH)_3CO = O(OH)_3H_2C_6$, the proportion of pyrogallic groups is 78·1 per cent., and the ratio of pyrogallol to tannin would be as 1 : 1·28, which is not in keeping with the results obtained by Mitchell.*

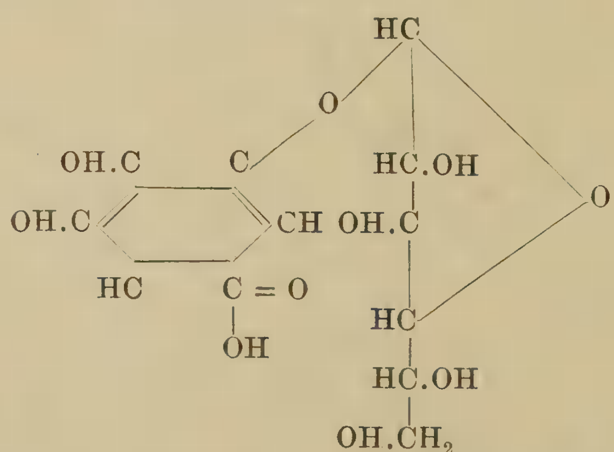
Nierenstein † obtained, by the acetylation of tannin, two distinct pentacetyl derivatives. One of these he regarded as a derivative of true tannin (digallic acid) with the formula given to it by *Schiff*, while to the other, which he termed *leucotannin*, he assigned the formula



This formula shows an asymmetrical carbon atom, CH(OH). Assuming commercial tannin to consist of a mixture or compound of these two substances, we should thus have an explanation of its optical activity.

In this communication *Nierenstein* expressed the opinion that glucose was not an integral part of the tannin molecule.

Feist ‡ extracted Aleppo galls with chloroform, benzene, and ether, and separated from the extract a compound which he termed *glucogallic acid*. This melted at 233° C., had a molecular weight of 315, and specific rotation in acetone solution of $[\alpha]_D = +10{\cdot}6°$. It was a monobasic acid, and, on hydrolysis with dilute acid, yielded 10 per cent. of gallic acid and 30 per cent. of dextrose. It had no action on *Fehling's* solution. When dried *in vacuo* its elementary composition was, $C_{13}H_{14}O_9$, and the following constitutional formula was attributed to it by *Guareschi*:—



* *Analyst*, 1923, xlviii., 3.
† *Ber.*, 1908, xli., 78, 3015.
‡ *Arch. Pharm.*, 1912, ccl., 668.

The residue left from the extraction of the galls was tannin. On hydrolysis it yielded gallic acid and dextrose, and had an optical rotation of $[\alpha]_D = 28 \cdot 6$ in acetone solution. Its molecular weight lay between 522 and 746, whilst that of the tannin from Chinese galls ranged from 879 to 1,045, as determined by the increase in the boiling-point of an acetone solution.

Iljin * obtained various compounds by fractionally precipitating with chloroform solutions of tannin in alcohol, ether, and ethyl acetate. The optical rotation was taken as the criterion of purity, the highest value obtained being $+76 \cdot 5°$. From the analyses *Iljin* drew the conclusion that none of these preparations was identical with digallic acid, which *Nierenstein* regarded as identical with tannin.

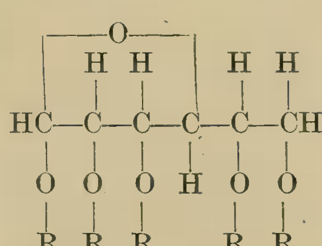
Herzig and *Renner* † prepared methylo-tannin from pure tannin. The specific rotation ranged from $[\alpha]_D = 7 \cdot 0°$ to $16 \cdot 05°$. When boiled with potassium hydroxide it yielded the trimethyl- and dimethyl-esters, the mixture of which was optically inactive.

The methoxyl content of methylated gluco-gallic acid was found by *Feist* and *Hahn* ‡ to correspond to a compound containing one molecule of dextrose and eleven or twelve molecules of gallic acid.

They also fractionated methyl-gallotannin into compounds corresponding with substituted glucoses containing 2, 3, and 4 galloyl groups.

In the meantime *Emil Fischer* § had prepared his pentadigalloyl glucose synthetically, and had shown that it closely resembled gallotannin in composition and in many of its characteristics.

The formula for this synthetic tannin is represented structurally as



where R represents the digalloyl group—

$$C_6H_2(OH)_3 . CO . O . C_6H_2(OH)_2CO.$$

* *Ber. d. d. Chem. Ges.*, 1909, xlii., 173.
† *Monatsh. Chem.*, 1909, xxx., 543.
‡ *Arch. Pharm.*, 1913, ccli., 468.
§ *Ber.*, 1912, xlv., 922; 1914, xlvii., 922; 1918, li., 1760; 1929, lii., 829.

This compound has a molecular weight of 1,700·4, and, containing five pyrogallic groups, its colorimetric ratio to pyrogallol would be as 1 : 2·72 (gallic acid = 1 : 1·81).

The specimens of gallotannin with which *Fischer* compared it were prepared by purifying commercially " pure " gallotannin by treatment with alkali and ethyl acetate. They were, therefore, fractionated compounds, and had an optical rotation similar to that of one of *Iljin's* fractions (*loc. cit.*). There is no evidence to show that they were typical of an average gallotannin not fractionated to such an extent. They yielded about 7 to 8 per cent. of glucose in the case of Chinese gall tannin, and about 12 to 14 per cent. in the case of Aleppo gall tannin.

Nierenstein * has criticised Fischer's formula for gallotannin on several grounds, and in particular because, when methylated and hydrolysed, gallotannin yielded tetramethyl-glucose, whereas Fischer's synthetic tannin, under the same conditions, yielded glucose.

This proved that in the case of the natural gallotannin four of the hydroxyl groups in the glucose molecule could not have been replaced by digalloyl groups.

The " long-chain " formula which *Nierenstein* proposes † as being more in keeping with the observed facts is that of a glucoside of a polydigalloyl-leuco-digallic acid anhydride—

$$
\begin{array}{l}
(OH)_3C_6H_2CO\,.\,[C_6H_2(OH)_3CO]x \\
\quad O\,.\,C_6H_2(OH)\,.\,CO\,.\,O\,.\,C_6H_2(OH)_2\,.\,CH(OH)\,.\,O\,.\,C_6H_2(OH)_2 \\
\qquad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\
\qquad O \text{———————————————————————} CO
\end{array}
$$

Omitting the glucose and taking x to represent unity, this compound would have a molecular weight of 779, and contain two pyrogallic groups, so that its colorimetric ratio (250 : 779) would be as 1 : 3·11. If a molecule of glucose were added, the molecular weight would become 959, and the ratio as 1 : 3·8.

The specimen of " pure " commercial gallotannin used by *Mitchell* as the standard tannin for his colorimetric method was a light, bulky powder of a pale cream tint, and contained 1·2 per cent. of moisture and 10·5 per cent. of gallic acid.

Its optical rotation in aqueous solution was $\alpha = +51{\cdot}8$. When exposed to the air for three weeks it absorbed 5 per cent. of moisture, and its optical rotation fell to $\alpha_D = +20$. This high optical rotation in aqueous solution indicated that its origin was Chinese

* *J. Chem. Soc.*, 1921, cxix., 275.
† *J. Soc. Chem. Ind.*, 1922, xli., 29T.

galls, since the tannin from Aleppo galls has a low rotation in aqueous solution ($\alpha_D = +2{\cdot}5$ to $+5$, *Fischer* and *Freudenberg*, *Ber.*, 1914, xlvii., 2495; 6·5, *Feist* and *Haun*, *Arch. Pharm.*, 1913, xxv., 524), whilst that of Chinese galls has a rotation varying up to about $\alpha_D = +73$, according to the extent of purification.

This gallotannin was very difficult to hydrolyse with acid—a characteristic of gallotannin noted by *Fischer* and by *Feist*. After being heated on the water-bath with 5 per cent. sulphuric acid and then left for 54 hours, it was treated with lead acetate to remove gallic acid and undecomposed gallotannin and the excess of lead precipitated with hydrogen sulphide; the filtrate contained no glucose. It was also hydrolysed with *Penicillium* for eight days and treated as before. The filtrate then showed an optical rotation of only $[\alpha]_D = +0{\cdot}2$, so that no material amount of glucose was present.

These results have since been confirmed by *Nierenstein*,* who has made a series of tests by the methods of *Fischer* and of *Feist* and *Haun*, and has not found more than 0·6 per cent. of glucose in this tannin.

Its high optical rotation in aqueous solution cannot, therefore, be attributed to its sugar content, and this remarkable result does not support *Fischer's* theory that gallotannin must be a glucoside of gallic acid.

The colorimetric comparison of this specimen of gallotannin with pure pyrogallol and gallic acid showed that it stood in a ratio of 1 : 3·32 to the former and of 1 : 2·22 to the latter.†

The results thus experimentally obtained agree fairly well with the theoretical value required by *Nierenstein's* formula (without glucose)—viz., 3·11—but do not agree with the value required by *Schiff's* formula or by that of *Fischer's* synthetic pentagalloyl glucose.

The general conclusion put forward tentatively by the writer is that the average "pure" tannin is a mixture of different glucosides, but mainly of didigalloyl glucose, with a digallic anhydride of the type described by *Nierenstein*.

A mixture of about one-third of such a substituted glucose with about two-thirds of *Nierenstein's* anhydride would yield the required proportion of glucose and contain the necessary pyrogallic groups, although, in the case of Chinese tannin, it would require the presence of a small amount of one of the higher substituted glucoses to raise the molecular weight to the observed value. This would not materially affect the colorimetric factor of 2·1 for Chinese galls,

* *Analyst*, 1923, xlviii., 321.

† *Analyst*, 1923, xlviii., 6.

which is in accordance with the results I have obtained with samples of those galls.

In the case of Aleppo galls there is a different mixture, having a lower molecular weight and giving a higher yield of glucose. Here there is apparently a considerably higher proportion of one or more of the lower substituted glucoses, and it is, therefore, reasonable to expect a somewhat lower colorimetric factor. This the writer has found to be in accordance with the facts. A factor of 2·1 gives in some cases results too high for the proportion of soluble extract, and a factor of 1·85 is required. It is obvious, therefore, that each tannin has its own average colorimetric factor.

FERMENTATION OF GALLOTANNIC ACID.—*Chevreul* showed that by keeping a solution of gallotannic acid in a sealed tube so as to exclude atmospheric oxygen, it remains unchanged for an indefinite period.

It was originally suggested by Scheele in 1778, and has since been repeatedly asserted (*e.g.*, by *Viedt*, p. 47), that the conversion of gallotannic acid is due to the action of an oxidising enzyme in the galls. It was shown, however, by *van Tieghem* * that this is not the case, but that the spontaneous change is due to the action of two mould fungi, *Penicillium glaucum* and *Aspergillus niger*, in the presence of air. By inoculating solutions of gallotannic acid with the spores of these fungi, he was able to effect a complete conversion of that substance into gallic acid in a few days. The fermentation only took place within the liquid, for when there was only a surface growth a very small amount of gallic acid had been produced after several days' vigorous fermentation. From the results of *Sacc's* † experiments it would seem that ordinary yeast also possesses the hydrolysing property of these two mould fungi.

The tannic acid fermentation has also been investigated by *Knudson*,‡ who has found that solutions of tannic acid are poisonous to many mould fungi, the only ones found capable of growing in 10 per cent. solutions of gallotannic acid being *Aspergillus flavus*, *A. niger*, *A. oryzœ*, and *Penicillium* species.

The fermentation produced by *A. niger* was more vigorous than that caused by *Penicillium* species. The addition of cane sugar protected the tannin from hydrolysis, but the presence of 10 per cent. of cane sugar did not inhibit the secretion of the specific enzyme, *tannase*, by *A. niger*, though it did to some extent that of *Penicillium*.

* *Comptes Rendus*, 1867, lxv., 1091.
† *Ibid.*, 1871, lxxii., 766.
‡ *J. Biol. Chem.*, 1913, xiv., 159.

The tannase secreted by *A. niger* is either more active or produced in greater quantity than that of *Penicillium*. The secretion of the enzyme in all the mould fungi is stimulated by the presence of tannic and gallic acids.

In this "fermentation" of gallotannin it was long assumed that the change taking place was simply the hydration of one molecule of gallotannic acid, or digallic anhydride, to form two molecules of gallic acid. Since, however, pure gallic acid was known to require only about half the proportion of iron required by gallotannin, the two gallic groups in gallotannin could only have one-half of the tinctogenic power of free gallic acid, if the old formula were correct.

If, however, the writer's theory of diluted pyrogallic groupings is correct (see p. 99), the two original groups in the gallotannin should appear again in the fermented product in a much more concentrated form, and in the correct proportion to agree with the formulæ for both substances.

In making tests to determine this question, two 0·1 per cent. solutions of the gallotannin (containing 10·5 per cent. of gallic acid)—*i.e.*, 0·895 gramme of gallotannin—were inoculated with moulds (*Penicillium*) which had formed on the surface of two stronger solutions, and the liquids exposed in loosely covered flasks at the ordinary temperature (60° to 65° F.). The flasks were shaken occasionally, and each day 1 c.c. of each solution was taken, and its colorimetric equivalent estimated in terms of pure gallic acid.

In each instance the hydrolysis proceeded to the anticipated extent, the gallotannin solution doubling its tinctogenic power in four to five days.

From this stage onwards, however, the solutions behaved differently, apparently owing to the action of the different mould fungi present. In each case there was first a gradual decrease in the tinctogenic power, while one solution turned progressively yellow, and the other remained nearly colourless.

In the case of the yellow solution this decrease continued until the liquid hardly gave any coloration with the reagent, whereas in the case of the other solution the colorimetric value, having reached the minimum corresponding with gallotannin, began to rise again, and continued in a state of unstable equilibrium.

The results thus obtained are shown in the following series, in which the values are expressed in comparison with a 1 per cent. solution.

Enzymic Hydrolysis of 0·1 per cent. Solutions of Gallotannin.

Results in Comparison with Gallic Acid as 100.

Days,	1	2	3	4	5	6	7	8	9	10
A. Gallic acid equivalent,	50	..	..	..	..	95	85	62	53	..
B. Gallic acid equivalent,	50	50	62	83	..	..	79	60	43	64

Days,	11	12	13	14	15	16	17	18	19	
A. Gallic acid equivalent,	..	49	..	42	37	30	..	..	15	
B. Gallic acid equivalent,	..	69	62	72	..	..	..	..	..	

In the first case, therefore, the hydrolysis proceeded practically to the complete destruction of the gallic acid formed, and in the second case the enzymic reaction appeared to be reversible.

Mr. *T. J. Ward* kindly made cultivations, on agar containing tannin, of the moulds from these two flasks. In the case of A gelatinous masses formed below the surface and nothing above, whilst B yielded typical mould growths on the surface.

Further experiments (*loc. cit.*) showed that gallic acid also undergoes enzymic hydrolysis, possibly with the formation of pyrogallol.

PROPERTIES OF GALLOTANNIC ACID.—Gallotannic acid is a yellowish-white, glistening, amorphous powder, which is readily soluble in water, alcohol, and ether.

When heated with dilute acids (*Stenhouse*) or fermented (*vide supra*) it takes up water and is converted into gallic acid, and when boiled with alkaline solutions it yields gallic and ellagic acids. When heated alone to 160° C. it is decomposed and yields a sublimate of pyrogallol (see p. 54). On reduction with zinc powder it yields diphenylmethane (*Nierenstein*).

It has a high optical rotation in aqueous solution, especially in the case of the gallotannin prepared from Chinese galls (see p. 43). Its molecular weight, determined by the boiling-point method, has been found to range from 600 to 800 for the tannin from Aleppo galls, and from 1,100 to 1,200 for Chinese gallotannin.

Gallotannic acid gives dark violet or blue precipitates with iron

salts. It is precipitated quantitatively by lead salts, with which it yields white compounds, and it forms white unstable gelatinous precipitates with antimony. It combines with gelatin to form an insoluble compound, such as is formed in the manufacture of leather.

The ordinary "pure" commercial gallotannic acid usually contains variable proportions of glucose either in the form of glucosides or firmly retained by adsorption. Particulars of a gallotannic acid containing less than 1 per cent. of glucose are given on p. 75.

Gallic Acid.

Gallic acid ($C_7H_6O_5 + H_2O$), which was discovered by *Scheele*, occurs normally in small proportion in various vegetable substances, such as tea, galls, and myrobalans (about 2 to 3 per cent.).

It is obtained from gallotannic acid by fermentation with certain mould fungi (p. 76), or by the hydrolysing action of dilute acids :—

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5.$$

Its constitutional formula shows that it may be regarded as benzoic acid, in which three atoms of hydrogen are replaced by hydroxyl groups :—

$$C_6H_2(OH)_3 \,.\, COOH + H_2O.$$

PROPERTIES.—Gallic acid crystallises in white silken needles, which melt above 200° C. It is much less soluble than gallotannic acid, 1 part requiring 130 parts at 12·5° C. to bring it into solution in water.

It is more soluble in absolute alcohol, 100 parts of which at 15° C. dissolve 27·95 parts, whilst 100 parts of ether at the same temperature only dissolve 2·5 parts.

When heated alone to about 215° C. it is decomposed, with the formation of pyrogallol ($C_6H_3.(OH)_3$) and water.

When heated with sulphuric acid at 100° C. it gives off red vapours of rufigallic acid, and under the influence of arsenic acid at a high temperature it yields ellagic acid.

It combines with alkalis to form salts, which, in alkaline solution, absorb oxygen from the air and turn brown.

Ferric salts are reduced by gallic acid, with the formation of blue-black compounds containing iron in the ferrous condition (*Chevreul*).

Gallic acid gives a ruby-red coloration with a 3 per cent. solution

of potassium cyanide. This disappears after some time, but reappears on shaking the liquid. Gallotannin and pyrogallol give yellowish-red colorations in this test (*Young*). The value of this test has been confirmed by *Fischer* and by *Nierenstein.*

Ferrous sulphate free from ferric salts gives no coloration with gallic acid, but ferric sulphate gives a blue colour and eventually a precipitate (*Wackenbroder*).

Unlike tannins, gallic acid does not yield an insoluble compound with gelatin.

It is decomposed by the enzymic action of mould fungi (*Mitchell*).

Various formulæ for the preparation of ink from gallic acid are given on p. 117.

REACTIONS DISTINGUISHING BETWEEN GALLOTANNIN AND GALLIC ACID.—It has been generally accepted that gallotannin gives black *precipitates* with ferric salts, and *no coloration* with ferrous salts,* but *Ruoss* † has shown that these statements are incorrect. He has found that gallotannin gives a black precipitate with ferric acetate, and a black precipitate or coloration with ferrous acetate.

Moreover, he has also proved that on adding a solution of a ferric salt, drop by drop, to a solution of gallotannin only a dark coloration (and no precipitate) is obtained, the iron tannate being readily soluble in an excess of tannic acid. Since gallic acid behaves in the same way, a dark coloration with ferric salts is inconclusive.

Ruoss has, therefore, devised the following two requests, which he has found to be both characteristic and very sensitive :—

Ruoss's Reagent I.—(1) Solution of 20 grms. of ferric sulphate per litre ; (2) solution of 28 grms. of crystalline sodium carbonate per litre ; (3) acetic acid (sp. gr. 1·04), containing 5 grms. of sodium tartrate per litre.

The tannin solution is diluted to such an extent that on adding the ferric sulphate solution drop by drop it still remains slightly transparent when the maximum colour has been reached. About 10 c.c. of such a solution are treated with the iron solution (1), which is added drop by drop until the colour ceases to become darker. The same number of drops of solution (2) are then added, and twice that quantity of solution (3). When the liquid is shaken and allowed to stand a black precipitate is obtained in the case of tannic acid, whilst gallic acid yields no such precipitate.

The reaction is capable of detecting 0·001 per cent. of gallotannin.

* *E.g.*, Schluttig and Neumann, *loc. cit.*, p. 18.

† *Zeit. anal. Chem.*, 1902, xli., 725.

Ruoss's Reagent II.—(1) A solution of 10 grms. of ferric sulphate + 15 grms. of sodium acetate + 1·7 grms. of sodium tartrate per litre; (2) a solution of 1·25 grms. of gelatin in 125 c.c. of hot water, made up to a litre with glacial acetic acid (sp. gr. 1·064).

Ten c.c. of the tannin solution are treated with solution (1), added drop by drop until the colour ceases to darken, and then with the same quantity of solution (2). After the liquid has been shaken and left for some time a flocculent blue-black precipitate indicates gallotannin.

*Ruoss's Oxidation Reaction.**—One drop of the ferric sulphate solution (20 grms. per litre) is added to 10 c.c. of the tannin solution, diluted as required in the test with Reagent I. A permanent dark coloration is obtained with gallotannin, whilst gallic acid gives a black coloration, immediately changing to yellow.

If ferric acetate is used instead of ferric sulphate the dark coloration is permanent with gallic acid as well as with gallotannin.

Griessmayer's Reaction † for gallotannin consists in adding one drop of a solution of tannin to a very dilute solution of iodine. The liquid becomes colourless, and on now adding a drop of a dilute solution of ammonia a blood-red colour is produced.

Ruoss has pointed out that the reaction is also given by gallic acid, and is, therefore, inconclusive.

Hydrogen Peroxide as a Reagent.—It was found by *Mitchell* that on adding hydrogen peroxide to a solution containing tannin and ferrous sulphate there is an immediate black precipitate, the tannin being precipitated quantitatively, or nearly so, as a basic tannate; whereas gallic acid treated in the same way yields a dark-brown solution, but only a slight trace of any insoluble compound. The precipitates yielded on ignition from 30 to 34·5 per cent. of ferric oxide, and thus approximated in composition to one of *Ruoss's* basic tannates (p. 90).

Mitchell has attempted to base a quantitative method of separating tannin on this reaction, but has been unable to obtain concordant results.

* *Loc. cit.*, p. 732.
† Classen, *Handbuch der qual. Anal.*, p. 163.

CHAPTER III.

NATURE OF INKS.

CONTENTS.—Constitution of ink-forming substances—Influence of light and air—**Iron tannates**—Evidence of an intermediate blue iron oxide—Tannates of iron—Basic salts—**Changes in ink on keeping**—**Methods of estimating tannates**—Procter's method—Jackson's lead carbonate method—Ruoss's ferric sulphate method—Titration with copper sulphate—with iodine—Colorimetric methods—Hinsdale's colorimetric method—Mitchell's colorimetric method—Ammonium molybdate method—Osmium tetroxide method—Extraction with ethyl acetate—Extraction apparatus.

CONSTITUTION OF INK-FORMING SUBSTANCES.—The property possessed by gallic and tannic acids of forming blue compounds with ferric salts was attributed by *Schiff* * to the presence of free phenoloid hydroxyl groups, to which is also due the analogous colorations obtained with other compounds of the aromatic series.

Thus, when a coloration is obtained with ferric chloride the presence of a free hydroxyl group may be inferred, and *vice versa*.

For instance, a *violet* coloration is given by phenol, salicylic acid, phenyl-sulphonic acid, etc.; a *blue* coloration by gallotannic acid, gallic acid, pyrogallol, arbutin, and many derivatives of tannic acid; a *green* colour by many tannins, æsculetin, and paræsculetin; a *red* or *reddish-violet* colour by phloridzin, tyrosin, etc.; whilst no coloration is obtained with picric acid, dinitro-hydroquinone, acetylgallic acid, etc.

Schiff also came to the conclusion that the intensity of the colour stands in relation to the number of free hydroxyl groups, the substances giving *violet* colorations containing only one free hydroxyl, whilst deep *blue-black* colorations are produced by compounds containing several free hydroxyl groups. Thus, phenyl-sulphonic acid, $C_6H_4\left\langle\begin{matrix}OH\\SO_2\,.\,OH\end{matrix}\right.$ gives a violet colour, and gallic acid, $C_6H_2(OH)_3\,COOH$, gives a blue-black colour.

* *Ann. Chem. Pharm.*, 1871, clix., 164.

Schiff's work was extended in a special direction by *Kostanecki*,* who investigated the relation between the constitution of certain organic dyestuffs and their tinctorial properties. He found that phenoloid colouring matters combine with oxide mordants when they possess two hydroxyl groups in the ortho position.

In a subsequent communication, *Kostanecki* † gave the name of "tinctogen group" to that atomic grouping which enables dyestuffs to combine with oxide mordants.

The further question of the formation of permanent "inks" upon vegetable fibres was thoroughly studied by *Schluttig* and *Neumann*.‡

In order to determine whether any phenol compound giving an intense coloration with iron salts was suitable for ink, they made a series of tests in which each substance was dissolved in water (with a little alcohol if required), and then treated with the same proportion of a solution of ferrous sulphate.

The liquids were allowed to run down white paper stretched at an angle of 45°, so as to form stripes 3 to 6 mm. in breadth as in their "Stripe test" (p. 159), which were then allowed to dry.

In the case of phenol, resorcinol, hydroquinone, phloroglucinol, orcinol, triacetylgallic acid, trimethyl-pyrogallol, and some other compounds, nothing but a faint yellow stain due to iron oxide was obtained.

On the other hand, dark violet colorations of varying intensity were given by gallic and tannic acids, pyrogallol-carboxylic acid, methyl and ethyl esters of gallic acid, potassium pyrogallol-sulphonate, and hæmatoxylin.

From these and similar experiments *Schluttig* and *Neumann* wrongly concluded that, in order to yield colours forming a permanent ink on paper, the compound must contain three hydroxyl groups in juxtaposition. For instance, hydroquinone $C_6H_4\begin{cases} OH \\ OH \end{cases}$ does not yield an ink, whilst gallotannin and gallic acid, each of which contains three adjacent hydroxyls, give permanent colorations.

The colorations produced by the other substances were as resistant to the action of water, and in some cases (*e.g.*, esters of gallic acid and hæmatoxylin) more resistant than the ordinary inks of gallic and tannic acids.

Influence of Light and Air.—On exposing stains given by the different compounds that formed inks for six weeks to the action

* *Ber.*, 1887, xx., 3146.
† *Ber.*, 1888, 3113, foot-note.
‡ *Die Eisengallustinten*, p. 16.

of a current of air and bright sunlight, the following results were observed :—

Completely bleached.—Colours of paroxybenzoic acid and ortho-carboxylic acid.

Yellowish-grey.—Pyrogallol-sulphonic acid, tribrompyrogallol, di-brom-gallic acid, and gallotannin.

Dark-grey.—Monobrom-gallic acid, pyrogallol-carboxylic acid, and gallic acid.

Dark Brown.—Pyrogallol.

Greenish, or *Bluish-black.*—Pyrocatechol, protocatechuic acid,* methyl and ethyl esters of gallic acid and hæmatoxylin.

From these results it appears that the inks of tannic and gallic acids are not the most permanent, but are far exceeded in this respect by logwood (hæmatoxylin) and other inks.

The behaviour of gallotannin ink was regarded remarkable, for it was the faintest of the colorations in its group; whereas if the then accepted formula, in which there are five hydroxyl groups, of which three at least are adjacent (see p. 71), had been correct, it should have been one of the darkest.

The stability of the inks was found to stand in proportion to their darkness on exposure.

The results obtained by *Mitchell* † in comparative tests with his ferrous tartrate reagent (see p. 99) point to the conclusion that the pyrogallic group is the tinctogenic agent both in gallic acid and in gallotannin. This would account for the difficulty noted by *Schluttig* and *Neumann*, for on this assumption the greater the proportion of the pyrogallic group in a substance, the darker the coloration which it will give with iron salts.

Schluttig and *Neumann* considered that these experiments showed conclusively that an estimation of gallic acid or gallotannin in an ink (as prescribed by the German statute of 1888, p. 14), without reference to the presence of other compounds of the same character, was of no value as a test of the permanency of that ink.

It has been shown by *Mitchell* ‡ that atomic groupings, found by *Schluttig* and *Neumann* to lead to the formation of iron inks, also applies to inks containing ammonium vanadate in place of iron, and to inks in which osmium tetroxide replaces iron.§

* In these two substances, pyrocatechol and protocatechuic acid, the molecules of which contain only two hydroxyl groups, Schluttig and Neumann themselves provide an exception to their rule; an analogous exception is to be found in the case of the inks formed with osmium tetroxide.

† *Analyst*, 1923, xlviii., 3.

‡ *Analyst*, 1903, xxviii., 146.

§ *Ibid.*, 1920, xlv.

IRON TANNATES.

COMPOUNDS OF IRON AND GALLOTANNIN.—Numerous metallic compounds of tannic acid have been prepared, but the iron salts are of primary importance in the manufacture of ink. Although nickel, cobalt, and manganese are so closely allied to iron, it is remarkable that none of them forms an "ink" with tannic acid.

On adding a ferrous salt to tannic acid no coloration is at first produced, though under the influence of the atmospheric oxygen the liquid speedily becomes violet, then darkens into an ink, and eventually deposits a violet-black compound (*vide infra*). On the other hand, when a ferric salt is added to a solution of tannic or gallic acid reduction takes place, and ferrous iron can be detected in the liquid (*Chevreul*).

EVIDENCE OF AN INTERMEDIATE BLUE IRON OXIDE.—*Berzelius* concluded that in these changes a new acid of blue colour was produced, but *Barreswil* * showed that the evidence pointed to the presence of compounds of tannic or gallic acid with an intermediate blue oxide of iron.

Thus, on mixing ferrous and ferric sulphate, and immediately placing the mixture in sulphuric acid to eliminate water, a deep blue mass is obtained. An evanescent blue sulphate is also produced by evaporating a solution of the two sulphates nearly to dryness. Similarly, by using crystalline sodium phosphate instead of sulphuric acid a deep blue iron phosphate is obtained. *Barreswil* was unable to isolate this blue oxide, but since the purest blue colorations were obtained with sulphuric acid, gallic acid, and sodium phosphate when the mixture contained three equivalents of ferrous salt to two equivalents of ferric salt, he inferred that the hypothetical blue oxide had the composition Fe_7O_9, or $3FeO \,.\, 2Fe_2O_3$.

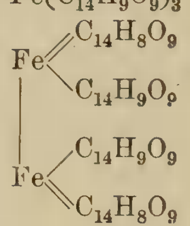
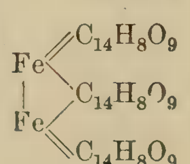
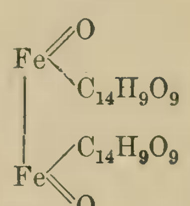
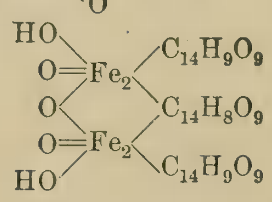
TANNATES OF IRON.—In 1833 *Pelouze* † studied the nature of the compound formed on adding *ferric* sulphate to a solution of tannin. The precipitate, when washed and dried at 120° C., yielded 12·0 per cent. of ferric oxide (= 8·4 per cent. of iron).

Wittstein ‡ prepared a series of insoluble compounds, but there is reason to doubt the individuality of some of these.

1. On leaving a solution containing $1\frac{1}{2}$ parts of tannin and one part of *ferrous* sulphate exposed to the air for a month, a precipitate with 8·40 per cent. of ferric oxide was obtained. This

* *Comptes Rendus*, 1843, xviii., 739.
† *Ann. de Chim. et Phys.*, 1833, liv., 337.
‡ *Jahresber. der Chem.*, 1848, xxviii., 221.

*Schiff's Formulæ for the Iron Tannates of Pelouze and Wittstein.**

Formula	Iron calculated. Per cent.	Ferric oxide calculated. Per cent.	Ferric oxide found. Per cent.
$C_{14}H_9(FeO)O_9$	14.21	20.3	20.15
$C_{14}H_7(FeO)_3O_9$	31.36	44.8	Wittstein prepared compounds containing 42.8 to 56.3 °/o
$C_{14}H_6(FeO)_4O_9$	36.95	52.8	
$C_{14}H_5(FeO)_5O_9$	41.36	58.99	
$Fe(C_{14}H_9O_9)_3$ — $Fe(C_{14}H_9O_9)_3$	5.53	7.9	8.4 (Wittstein)
	8.00	11.5	12.0 (Pelouze)
	10.43	14.9	13.4, 14.9, 15.4 (Wittstein)
	14.21	20.3	20.15 (Wittstein)
	17.63	25.2	25.0 (Wittstein)

* See also a formula on p. 111, suggested by Schiff, which corresponds better with the amount of iron found by *Wittstein*, and by *Mitchell*.

is apparently the substance formed when ink dries on paper (see *Mitchell, infra*).

2. From a solution containing three parts of tannin to one part of ferric acetate a precipitate yielding 20·15 per cent. of ferric oxide was obtained.

3. On diluting the dark blue solution a resinous precipitate with 13·49 per cent. of ferric oxide resulted.

4. Tannin solution added drop by drop to ferric acetate solution gave a precipitate yielding 50 per cent. of ferric oxide.

5. On adding ferric acetate solution to a tannin solution the precipitate yielded 25 per cent. of iron oxide.

*Schiff** pointed out that the series of salts described by *Wittstein* might be grouped into two series—viz., those in which the hydrogen in a molecule of acid might be regarded as being replaced by the monovalent group—[FeO], and those in which several molecules of the acid gradually replaced the hydroxyl groups in ferric hydroxide —$Fe_2(OH)_6$.

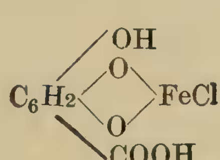
Schiff considered it doubtful whether some of *Wittstein's* gelatinous deposits were individual compounds, but at the same time pointed out that the agreement between the theoretical values and the results actually obtained was remarkable.

Viedt † stated that he had prepared an iron tannate containing 17·8 grms. of iron to 100 grms. of tannin, but gave no details of the analysis.

Schluttig and *Neumann's* and *Mitchell's* experiments on the composition of the spontaneous deposit from a solution of ferrous sulphate and tannic acid are described at length below.

The experiments of *Raschig* ‡ indicated that the iron in iron tannates is not directly united to the carbon atom, but that it takes the place of hydrogen in the phenolic-hydroxyl group.

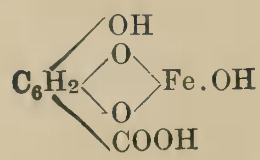
IRON GALLATES.—*Silbermann* and *Ozorovitz* § concluded that the interaction of gallic acid and ferric chloride yields a *chloroferrigallic acid,* to which they assigned the formula :—



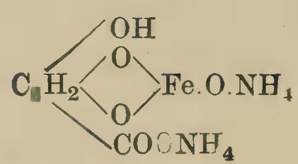
This acid dissociates on standing, yielding gallic acid and ferric

* *Ann. Chem. Pharm.*, 1875, clxxv., 176.
† *Dingler's polyt. Journ.*, 1875, ccxvi., 456.
‡ *Zeit. angew. Chem.*, 1907, 2065.
§ *Chem. Zentralbl.*, 1908, ii., 1024.

chloride, and when treated with ammonia gives an ammonium salt —*ammonium ammonium oxyferrigallate*—



which is precipitated, and then, on addition of excess of alkali, is redissolved, forming a bluish-violet solution. Then, by adding alcohol, the *hydroxy-ferrigallic acid* is precipitated in blue flakes—



which have the same composition as the substance formed on treating gallic acid with ferric hydroxide (*infra*).

Ammonium gallate solutions, when shaken with ferric hydroxide, give the deep red slightly soluble salt of hydroxy-ferrigallic acid, and this, on addition of ammonia, forms a readily soluble ammonium ammonium oxyferrigallate.*

The latter salt can also be prepared directly by shaking ammonium gallate solution with ferric hydroxide and ammonia.

Other compounds containing at least two OH-groups, or one OH-group and one COOH-group in the ortho position, yield similar salts—the iron-ammonium compounds all being soluble in water (bluish-red solutions) and precipitated by alcohol.

The tannic acid salt is insoluble in water containing 10 per cent. of alcohol. Alkali carbonates or alkaline-earth hydroxides may

* While this book was in the press an investigation of the iron compounds formed in writing inks was published by *Zetsche* (*Annalen*, 1923, 434. 233). Doubt is expressed as to the purity of the compounds described by *Silbermann* and *Ozorovitz*; and it is concluded that the following changes take place when ink is applied to paper:—(1) A neutralisation process, in which pale green ferrous compounds, partly soluble (ferrous digallate) and partly insoluble (ferrous monogallate and ferrous tannate), are formed. (2) These ferrous salts are oxidised by atmospheric oxygen into the bluish-violet primary ink salts (probably ferric monogallate and penta-ferric tannate). (3) Under the further influence of air and moisture these salts undergo decomposition of their carboxyl and ester groups, with the liberation of carbon dioxide, and are converted into secondary ink salts of brown colour, which appear to be identical with salts of pyrogallol.

take the place of ammonia in the formation of these complex compounds with iron or other metals.

INK FROM AMMONIUM AMMONIUM OXYFERRIGALLATE.—The compound isolated by *Silbermann* and *Ozorovitz* may be used as a writing ink in a 7 to 8 per cent. solution. The writing is violet-black at first, but becomes black in a few hours, and the deposit upon the paper is sufficiently oxidised in 30 minutes not to be removable by water.

Basic Salts.—*Ruoss* * described a basic iron tannate, consisting of a previously unknown ferric tannate in combination with ferric hydroxide.

This was prepared by treating a tannin solution with the sodium carbonate solution, and adding ferric sulphate solution to the soluble sodium tannate formed. The excess of iron could be removed by treating the basic tannate with normal acetic acid, leaving the insoluble ferric tannate.

This, when dried at 100° to 120° C., contained 15·0 per cent. of iron, as against 14·9 per cent. required by a tannate of the formula—

$$(C_{14}H_7O_9)\ Fe.$$

Taking into consideration the formation of other basic salts, *Ruoss* subsequently came to the conclusion that it must be regarded as tannin in which the hydrogen of the carboxyl group was replaced by the monovalent group [FeO], thus—

$$C_{14}H_9O_9(FeO) = C_{14}H_7O_9Fe + H_2O.$$

Similar black basic salts, containing two, three, four, or five atoms of iron in the molecule, were prepared, but when more iron was introduced the colour became brownish-black.

These salts may be regarded either as compounds of the normal tannate $(C_{14}H_7O_9)Fe$, with ferric hydroxide, or as compounds in which the group [FeO] replaces hydrogen, both in the carboxyl group and in the hydroxyl of the ferric hydroxide, *e.g.*—

$$(C_{14}H_7O_9)Fe + 3Fe(OH)_3 = (C_{14}O_9H_6)(FeO)_4 + 5H_2O.$$

We give the amount of iron in these basic salts dried at 100° C., so that they may be more readily compared with compounds of *Wittstein* and other earlier investigators.

* *Zeit. anal. Chem.*, 1902, xli., 732.

Basic Tannates of Ruoss.

Formula.	Iron. Per cent.	Ferric oxide. Per cent.	Iron found. Per cent.
$(C_{14}H_7O_9)Fe$	14.9	21.27	15.0
$(C_{14}H_7O_9)(FeO)_2$	24.42	34.88	—
$(C_{14}H_7O_9)(FeO)_3$	31.40	44.85	—
$(C_{14}H_6O_9)(FeO)_4$	36.96	52.79	—
$(C_{14}H_5O_9)(FeO)_5$	41.36	58.99	—

Since the composition of these basic salts varies with the concentration of the iron solution used for the precipitation, *Ruoss* points out that they may also be regarded as merely mixtures of the normal tannate with ferric hydroxide.

Ruoss has based a method of determining tannin upon its precipitation as the tannate $(C_{14}H_7O_9)Fe$ (*vide infra*).

Iron Tannate precipitated by Hydrogen Peroxide. — *Mitchell* has investigated the nature of the tannate formed on adding hydrogen peroxide to a solution containing tannin and ferrous sulphate. There was an immediate dense black precipitate, which rapidly subsided, leaving a colourless solution. The precipitates thus obtained, when dried at 100° C., were found to contain 21 to 22·5 per cent. of iron, and were probably basic tannates.

Gallic acid treated in the same manner yielded only a very slight deposit, but the colour of the solution changed to dark reddish-brown.

As already mentioned, attempts to base a quantitative method of estimating gallotannic acid on this reaction have so far proved unsuccessful.

CHANGES IN INK ON KEEPING.—The deposits which form gradually in finished ink, when kept in flasks protected from the action of the air, have commonly been regarded as iron tannates, but experiments made by *Hinrichsen** show that this is not the case.

Six samples of ink were kept for three years in flasks, and the proportions of gallotannic and gallic acids and of iron were estimated before and after this treatment, with the following results :—

* *Die Untersuchung von Eisengallustinten* (1909), p. 124.

	Gallotannic and gallic acids. Grms. per litre		Iron. Grms. per litre	
	1904	1907	1904	1907
1	50.5	23.9	7.6	7.5
2	49.6	42.1	7.5	7.7
3	46.0	37.7	7.6	7.7
4	40.7	35.5	3.9	3.9
5	36.4	20.9	7.2	7.3
6	33.4	28.8	4.5	4.6

These striking results show that, while the iron kept fairly constant, there was a pronounced decrease in the proportion of gallotannic and gallic acids in the inks, and that the deposits could, therefore, have contained very little iron.

This conclusion was confirmed by estimation of the iron in the deposits, when the following amounts were found:—(1) 0·40; (2) 0·70; (3) 0·28; (4) 0·31; and (5) 0·60 per cent.

The deposits were, therefore, not iron tannates, but probably consisted of condensation and oxidation products of gallotannic and gallic acids.

These results also indicate that an ink may fall below a standard quality when kept in a closed flask.

Methods of Estimating Tannin.

The methods of estimating tannins are very numerous, and attempts have been made to utilise most of the reactions that seemed likely to give anything approaching quantitative results. Thus precipitation with gelatin * and all kinds of metallic salts has been tried, but the results of different observers have been far from concordant, which must be largely attributed to the fact that there are numerous tannins, and that these vary in their behaviour with different chemical reagents.

For valuation of tannin materials for leather manufacture the methods chiefly used are *Löwenthal's* method, which is based on the reduction of potassium permanganate by tannins, and *Procter's* method, which depends on the absorption of the tannin by purified hide powder.

* *Spiers* has shown that caseinogen can be used as a precipitant in place of gelatin.

In the permanganate method an aqueous solution of the tannin material is first titrated with potassium permanganate solution, with indigo carmine as indicator, to obtain a valuation of all the reducing substances present. The tannin is then precipitated by means of gelatin, and the filtrate again titrated, the difference

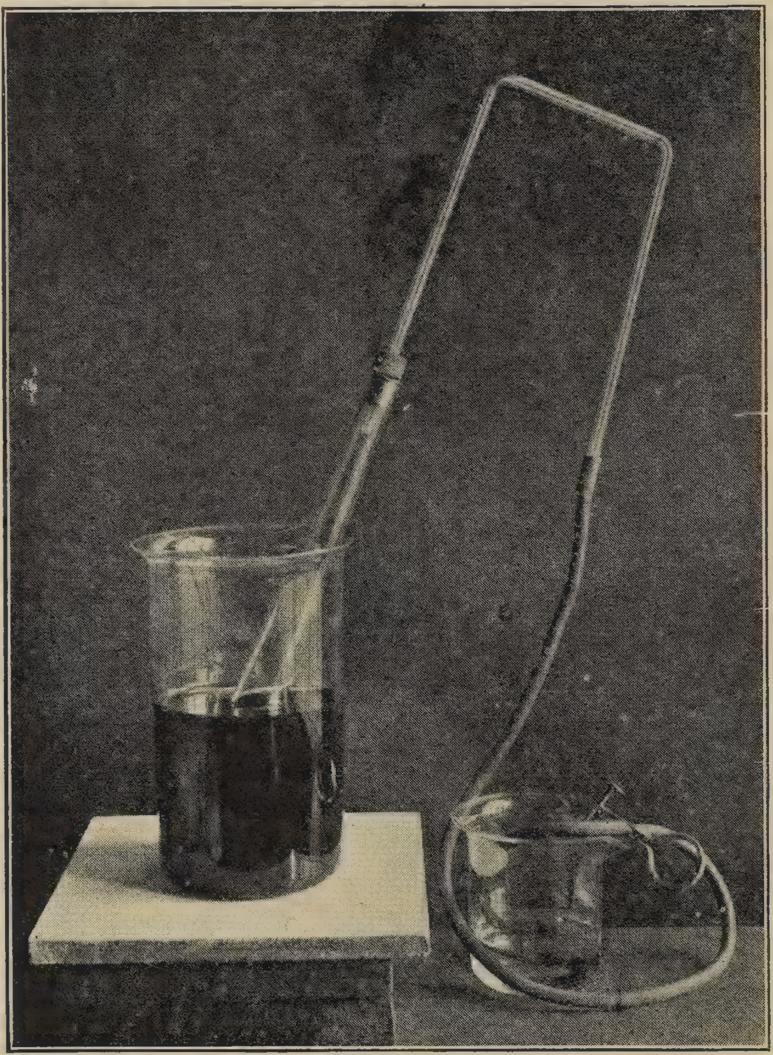


FIG. 33.—Trimble's apparatus for tannin determination.

between the two results giving the amount of tannin in terms of potassium permanganate. The method will thus give the relative tanning value of two samples of the same kind of material, but numerous precautions are essential; for the speed of titration, strength of the solution, and other factors, have an influence on

the results. This method, which does not estimate gallic acid or other compounds (other than tannin) that give a coloration with iron salts, is an unsuitable one for the valuation of tannin material for ink manufacture.

PROCTER'S METHOD.—We have found *Trimble's* * apparatus (Fig. 33) a very simple and satisfactory one for the estimation of tannin by *Procter's* method. It consists of a cylinder of about 500 c.c. capacity, and a funnel-shaped tube about 18 cm. in length, and 2·5 cm. in width at the bottom, whilst the other end tapers to a fine tube, on which is fixed a piece of flexible rubber tubing to form the other limb of the siphon.

A small piece of cotton wool is pushed lightly down to the narrow end, and the tube then loosely packed with 8 to 10 grms. of purified hide powder, and the opening closed with a large piece of cotton wool.

The tannin infusion is poured into the cylinder a little at a time, so as gradually to moisten the hide powder. After standing for about two hours the liquid is gently siphoned through the india-rubber tube, the first 30 to 40 c.c. being rejected. Fifty c.c. of the filtrate are then evaporated to dryness on the water-bath, the difference between the weight of the residue and that previously obtained by evaporating 50 c.c. of the tannin before the filtration giving the amount of tannin absorbed by the hide powder.

Trimble obtained results by this method higher than those given by the permanganate and alum gelatin methods.

The method should be employed by the ink manufacturer in conjunction with a colorimetric one, since it does not estimate any gallic acid present.

JACKSON'S LEAD CARBONATE METHOD.†—This is based upon *Jackson's* determination that a 1 per cent. aqueous solution of gallotannic acid has a specific gravity of 1,003·8 at 15·5° C.

The extract or decoction of the substance is diluted to a litre, and its specific gravity determined at 15·5° C. (*e.g.*, 1,003·86). It is then shaken with dry lead carbonate at intervals for two or three hours, after which it is filtered and the specific gravity of the filtrate determined. The loss in specific gravity (*e.g.*, 1,003·86 − 1,001·52 = 2·34) divided by 3·8 and multiplied by 20 gives the percentage of tannin absorbed by the lead (*e.g.*, in this case = 12·30 per cent.).

Jackson obtained the following results with solutions of 5 per cent. strength :—

* *The Tannins*, ii., p. 98.

† *Chem. News*, 1884, l., 1079.

	Specific gravity of solution.	Specific gravity of filtrate.	Tannin Per cent.
Valonia	1009.08	1003 33	30.2
Sumach	1008.25	1003.61	24.4
,, ...	1009.61	1005.08	23.8
Oak-wood extract . .	1007.33	1003.15	21.9
Chestnut wood extract .	1006.06	1002.48	18.8

The filtrate from the lead precipitate in this method forms a black ink with iron salts, and the method is unsuitable for valuing tannin materials for ink manufacture, unless used in conjunction with a colorimetric method.

RUOSS'S FERRIC SULPHATE METHOD.*—This is based upon the formation of sodium tannate and the subsequent precipitation of the tannic acid as the compound $C_{14}H_9O_9$ [FeO] (*vide supra*) by means of a solution of ferric sulphate containing sodium tartrate, to prevent spontaneous formation of basic ferric oxide, and acetic acid to dissolve the ferric hydroxide, which would otherwise be precipitated simultaneously with the tannic acid.

The reagents required are: (1) a solution of 50 grms. of ferric sulphate (or an equivalent quantity of ferric chloride or ferric ammonium sulphate) per litre; (2) a semi-normal solution of crystalline sodium carbonate (71·3625 grms. per litre); and (3) a solution of 5 grms. of sodium tartrate in a litre of dilute (6 per cent.) acetic acid.

It is essential that the ferric sulphate should be at least equivalent to the sodium carbonate solution—*i.e.*, when 10 c.c. of each are boiled together and filtered, the filtrate must not give an alkaline reaction with methyl orange. In preparing it the liquid must not be boiled, or basic iron compounds will be deposited.

A further test to be applied to the solutions is that on mixing 50 c.c. of water, 10 c.c. of solution (1) and 10 c.c. of solution (2), and immediately adding 25 c.c. of solution (3), the liquid must remain perfectly clear after being boiled for five minutes.

The tannin solution may be neutral or faintly acid or alkaline, but must not contain more than 0·4 per cent. of tannic acid.

In the estimation 50 c.c. of such a solution are shaken with 10 c.c. of solution (2) and 10 c.c. of reagent (1) (an evolution of carbon dioxide taking place), and then *immediately* mixed with

* *Zeit. anal. Chem.*, 1902, xli., 717.

25 c.c. of the sodium tartrate solution (3), well shaken, and boiled for five minutes. It is filtered, and the precipitate washed until the washings are free from iron, and then dried, ignited, and weighed.

The weight of the residue multiplied by the factor

$$\frac{321 \cdot 22 \,.\, 0 \cdot 7001}{56} = 4 \cdot 024$$

gives the amount of tannic acid (mol. weight $= 321 \cdot 22$) in 50 c.c. of the tannin solution.*

Gallic acid treated in the same way gives a brown coloration, but no precipitate, with the reagents, and passes into the filtrate, where it might be estimated colorimetrically.

This method has not proved satisfactory in our hands as a means of determining the value of tannin material for the manufacture of ink; and, although closely following the directions given, we have been unable to obtain concordant results in experiments with solutions of gallotannic acid.

HINRICHSEN'S COPPER SULPHATE TITRATION METHOD.† —The residue from the extraction of the ink with ethyl acetate is treated with a measured excess of standard copper sulphate solution in the presence of calcium carbonate, and the excess of copper solution titrated with a standard solution of pure gallotannic acid, the end point being found by spotting on filter paper with potassium ferrocyanide. The most convenient strength for the copper sulphate solution is 100 grms. of the crystalline salt per litre, while the gallotannic acid solution should contain 25 grms. per litre.

Gallic acid consumes approximately twice as much copper solution as the same weight of gallotannic acid. This is explainable on the assumption that it is mainly the carboxyl groups that react.

In practice, however, the readiness with which gallic acid oxidises causes the proportion to be somewhat smaller —viz., 1·8. Taking this as the factor, the relative amounts of gallotannic and gallic acids in the weighed extraction residue may be calculated from the results of the titration by means of the formula

$$\begin{aligned} x + 1{\cdot}8y &= a \\ x + y &= b \end{aligned}$$

where x represent the gallotannic acid, y the gallic acid, and a the quantity of gallotannic acid corresponding to the amount of copper sulphate solution used.

* This molecular weight is not in accordance with the results of more recent investigations of gallotannin (see p. 71).

† *Die Untersuchung von Eisengallentinten* (1909), 80.

The weak point about the method is that "pure" gallotannin is of so variable a composition that no two preparations are likely to give the same values. It would be preferable to base the calculation upon pure gallic acid until the constitution of gallotannin has been definitely established.

Hinrichsen bases his formula upon the now obsolete theory that gallotannic acid is the anhydride of gallic acid.

TITRATION WITH IODINE.—The method of titrating the residue with iodine is described on p. 169. It gives results in agreement with those obtained by the copper sulphate method.

One molecule of gallotannic acid absorbs approximately 16 atoms of iodine, and one molecule of gallic acid absorbs 8 atoms of iodine in the presence of sodium bicarbonate.

Here, again, the same criticism as to the variable composition of gallotannic acid is applicable.

COLORIMETRIC METHODS.—It is obvious that the ordinary gravimetric methods used by the leather manufacturer for the valuation of tannic materials are not very suitable for the purposes of the ink manufacturer, who wishes to take into account all the substances capable of forming coloured compounds with iron salts, and not merely those forming insoluble compounds with gelatin.

The filtrate from the estimation of tannin by *Procter's* method almost invariably gives a dark colour with solutions of ferric salts, and this is more marked in the case of samples of old material in which the original gallotannin has undergone more or less decomposition. For instance, *Mitchell* has found old English oak-marble galls to contain 11 per cent. of tannin by the gelatin absorption method, whereas the filtrate from the gelatin compound gave a deep blue-black colour with ferric salts, and when tested by his colorimetric method was found to contain substances equivalent in tinctorial effect to an additional 18 to 19 per cent. of gallotannin (see also p. 51).

HINSDALE'S COLORIMETRIC METHOD.—*Hinsdale** has described a method in which the reagent is prepared by dissolving 0·04 grm. of potassium ferricyanide in 500 c.c. of water and adding 1·5 c.c. of ferric chloride solution (Amer. Pharm. strength).

The standard tannin solution consists of 0·04 grm. of "pure" gallotannic acid dried at 100° C.

In estimating the proportion of tannin in, *e.g.*, oak bark, 0·8 grm. of the sample is extracted with successive quantities of boiling water, and the extract made up to 500 c.c. Five drops of this

* *Amer. J. Pharm.*, 1890, lxii., 119.

extract are then treated with 5 c.c. of the reagent, and the same quantity added to 4, 5, 6, 7, and 8 drops of the standard tannin solution. After one minute 20 c.c. of water are added, and the colours matched within three minutes.

Hinsdale asserts that the method is applicable to any substance containing less than ten per cent. of tannin. In the case of stronger solutions an equal volume of water must be added and the results multiplied by 2.

The writer has made a series of estimations by this method, but in his opinion it has the drawbacks that the reagent, in addition to being unstable and possessing too dark a colour, gives somewhat indecisive colorations with tannin, which are not easy to match. Moreover, "pure" gallotannic acid is not sufficiently uniform in composition to be used as a general standard.

These objections do not apply to the following colorimetric process.

MITCHELL'S COLORIMETRIC METHOD.*—The reagent consists of a solution of 0·1 grm. of ferrous sulphate and 0·5 grm. of sodium potassium tartrate (Rochelle salt) in 100 c.c. of water. On adding this to a dilute solution of gallotannic acid, gallic acid or pyrogallol a violet coloration is produced, the intensity of which is proportional to the amount of these acids present.

The standard solution for colorimetric comparison consists of a solution of pure pyrogallol or gallic acid and the whole of the substances giving a coloration with the reagent are expressed in terms of either compound.

The coloration varies with the proportion of the reagent to tannin substance. If the reagent is in excess the coloration is a reddish-violet, whilst if the tannin is in excess it is a bluish tint. It is preferable to adjust the proportions in such a way that an intermediate violet coloration is produced. When once formed, no subsequent dilutions of the solution will change any of these three coloured compounds into either of the others.

The reagent should be freshly prepared and added to the tannin solution, which may afterwards be diluted to match the standard. The violet coloration is still perceptible in a solution containing 0 0001 grm. of gallic acid in 100 c.c.

The reagent does not give any coloration with phenol or other monohydroxylated compounds, nor with salicylic acid or certain other compounds containing two hydroxyl groups. Apparently the violet colour is specific for the pyrogallic grouping in neutral solution, and affords a measure of that group in different compounds.

* *Analyst*, 1923, xlviii., 2.

Quantitative Colorimetric Comparisons.—As mentioned above, either pure pyrogallol or pure gallic acid may be used as the standard for the comparison, but gallic acid is preferable, since it is more stable in solution. It is convenient to use a solution of 0·1 grm. of either substance in 100 c.c. of water and make (Fig. 34) the comparison in Nessler tubes provided with Hehner's side

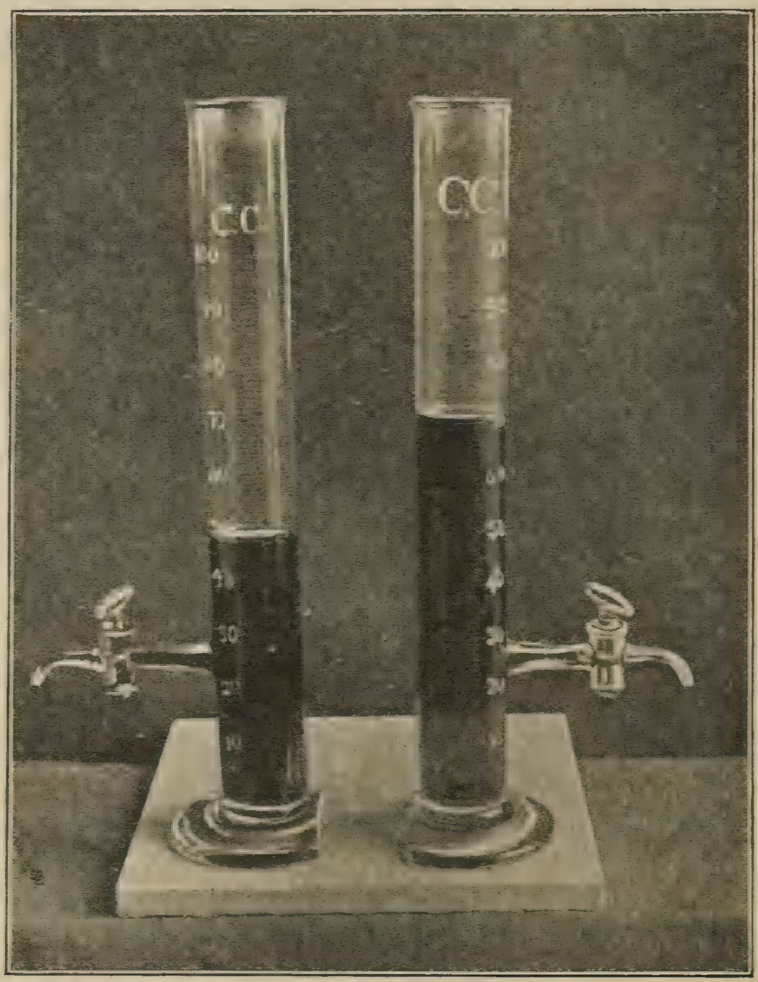


FIG. 34.—Hehner's Nesslerising Tubes.

tubulures and taps. In the case of gallotannin or gallic acid, 0·1 grm. of the substance is also dissolved in 100 c.c. of water, and 1 c.c. of each solution is added to about 95 c.c. of water in the respective cylinders. Two c.c. of the reagent are then added to each tube, the solution made up to 100 c.c., and the colours compared both vertically and horizontally. If the colours are both dark, the contents of the tubes are run down to 50 c.c., the colours

again compared, and the darker liquid then run out until the colours match. The contents of both cylinders are then diluted to 100 c.c. and again compared at different levels. If the solution of the unknown substance is so dilute that it gives the reddish-violet colour mentioned above, the estimation should be repeated with only about a third of the quantity of the gallic acid solution in the standard tube prior to the addition of the reagent.

The coloration is so stable that the process of dilution and comparison of the liquids at different levels can be repeated several times without recharging the tubes. Not infrequently the ferrous tartrate is sufficiently acid to prevent any coloration appearing. In such cases the use of tap water will neutralise the acidity, or, if preferred, a measured quantity of N/10 sodium carbonate solution may be added prior to the reagent.

Comparison of Pyrogallol with Gallic Acid.—In test experiments the same rich violet coloration was given by each substance on the addition of the reagent, but the 65 c.c. of the dilute pyrogallol solution had to be diluted to 100 c.c. to match the 100 c.c. of gallic acid solution. That is to say, the ratio between the two compounds was 1 : 1·53. The gallic acid lost 9·3 per cent. of water of crystallisation at 100° C. (theoretical amount 9·5 per cent.), and the solution of anhydrous acid (100 c.c.) was then matched by 74 c.c. of the pyrogallol solution (Ratio = 1 : 1·35).

Now if we compare the molecular weights of the three substances, we get the following ratios :—

		Molecular Weight.	Ratio.
Pyrogallol,	$C_6H_2(OH)_3 . H$, . .	125	1
Crystalline gallic acid,	$C_6H_2(OH)_2 . COOH + H_2O$,	188	1·50
Anhydrous gallic acid,	$C_6H_2(OH)_2 . COOH$, . .	170	1·36

In each instance, therefore, the pyrogallic group, $C_6H_2(OH)_3$, is the tinctogenic agent, and the carboxyl group and the water of crystallisation act merely as diluents of that group.

Comparison of Gallotannin with Pyrogallol.—One c.c. of a 0·1 per cent. solution of the "pure" commercial gallotannin already described (p. 74) was diluted to 100 c.c., and then required 33·5 c.c. of the standard pyrogallol solution to match the colour produced by the reagent. The 10·5 per cent. of gallic acid in the

gallotannin was colorimetrically equivalent to 7 per cent. of pyrogallol. Hence:

Gallotannin. Grm.	Gallotannin (after deducting 10·5 % gallic acid). Grm.	Pyrogallol. Grm. Grm.
0·1	0·0895	= 0·0335 – 0·0070
		= 0·0265

Ratio = 1 : 3·37, or, allowing for 1·2 per cent. of moisture in the tannin, 1 : 3·32.

Comparison of Gallotannin with Gallic Acid.—A series of estimations made on different occasions and with freshly prepared solutions (with deductions as before for the 10·5 per cent. of gallic acid in the tannin) gave results of which the following are typical:—

1. Gallotannin.		Gallic Acid.
0·1 grm., less 0·0105 grm. = 0·0895 grm.	=	0·05 grm. (less 0·0105 grm.) = 0·0395 grm.
Ratio = 1 : 2·26.		

These results are consistent with those previously obtained by comparison with pyrogallol (2·22 × 1·5 = 3·33).

This factor proved satisfactory for the estimation of tannin in Chinese galls, from which this particular tannin was derived, but was too high in the case of Aleppo galls (see p. 42). Each tannin apparently has its own colorimetric factor.

Analysis of Commercial Gallic Acids.—Two samples of technical gallic acid were tested in comparison with pure gallic acid. The first was a dark buff powder containing 11·36 per cent. of water, and the other a dirty grey powder with 11·49 per cent. of water. The first corresponded with 76 per cent. of the pure acid, and the second with 97 per cent. A third sample matched the standard exactly and was therefore of 100 per cent. purity.

Estimation of Gallotannin in the presence of Gallic Acid.—The two substances are first estimated together in terms of gallic acid, the gallotannin then precipitated, *e.g.*, with quinine hydrochloride, and the gallic acid in the filtrate again estimated. The difference between the two results, multiplied by the appropriate factor, gives the amount of gallotannin.

Precipitation with quinine sulphate was made the basis of a gravimetric method of estimating tannin in tea by *Tatlock and Thompson*,* but the objection to that method is that colouring matters are also precipitated simultaneously with the tannin, and that the composition of the precipitate will therefore vary with the

* *Analyst*, 1910, xxxv., 104.

nature of the original material. In the case of the colorimetric method the removal of colouring matters is an advantage, and the the presence of quinine in the filtrate does not interfere with the colour reaction.

Estimation of Gallic Acid in Gallotannin.—In the test experiments with the "pure" specimen of gallotannin, 0·1 grm. was equivalent colorimetrically to 0·05 grm. of gallic acid. Ten c.c. of the 0·1 per cent. solution were then treated with a slight excess of a solution of quinine hydrochloride, the precipitate filtered off after about five minutes, and washed several times with water (about 25 c.c. in all), and the filtrate and washings made up to 100 c.c. Ten c.c. of this solution (corresponding with 1 c.c. of the original solution) were then compared, as before, with the standard, and the following results were obtained:—

Gallotannin, 0·1 grm.	matched	Gallic acid, 0·05 grm.
Filtrate from 0·1 grm.	matched	Gallic acid, 0·0105 grm.

Amount of gallic acid = 10·5 per cent.

Mixtures of Gallotannin and Gallic Acids.—The following results were obtained with test mixtures of this gallotannin and pure gallic acid, the gallotannin in each case being multiplied by the empirical factor 2·2:—

MIXTURES OF GALLOTANNIN AND GALLIC ACID.

Gallotannin Grm.		Gallo-tannin (less 10·5 % of gallic acid) Grm.	Gallic acid Grm.		Gallic acid + 10·5 % Grm.	Gallic acid Equiv. of Mixture. Grm.	Gallic Acid Equiv. of Filtrate. Grm.	Difference. Grm.	Tannin (Difference × 2·2). Grm.
0·05	=	0·0447	0·05	=	0·0553	0·078	0·058	0·020	0·0440
0·05	=	0·0447	0·05	=	0·0553	0·075	0·056	0·019	0·0418
0·025	=	0·0221	0·075	=	0·0779	0·087	0·076	0·011	0·024
0·010	=	0·0085	0·090	=	0·0910	0·095	..	0·004	0·0088

Making allowance for the fact that the gallotannin was not a pure substance, these results are sufficiently accurate to prove that the method may be regarded as trustworthy.

Commercial Tannic Acids.—A sample of technical tannic acid was of a pale brown colour and contained 10·8 per cent. of moisture. The total gallic acid equivalent of 0·1 grm. was 0·0350 grm. and the gallic acid equivalent of the filtrate from the quinine precipitation was 0·0081 grm.

Hence the gallotannin $= (0 \cdot 0350 - 0 \cdot 0081) \times 2 \cdot 1 = 56 \cdot 49$ per cent.; and the gallic acid $= 8 \cdot 1$ per cent.

In the case of another commercial sample the following results were obtained:—Total gallic acid equivalent, 35 per cent.; gallic acid in filtrate, 8·1 per cent.; tannin $(26 \cdot 9 \times 2 \cdot 1) = 56 \cdot 4$ per cent.

A third sample, which was about 15 years old, contained 10 per cent. of moisture and 16·2 per cent. of an insoluble reddish compound. The soluble matter consisted of 4·5 per cent. of gallic acid and 79·6 per cent. of tannin. Total constituents estimated $= 100 \cdot 3$ per cent.

Effect of Colouring Matters.—Certain products, such as roasted galls or myrobalans, yield a deep yellow extract which, even in very dilute solution, gives a slight yellow tint, and so modifies the colour produced by the reagent.

In such cases the simplest plan is to tint the standard solution with caramel until it matches the solution under examination, prior to the addition of the reagent.

Another, and preferable, method is to attach a Lovibond tintometer glass of the right tint in the 52 series, by means of rubber bands, to the bottom of the Nessler cylinder.

For other results obtained by the use of this method with galls, myrobalans, and divi-divi see pp. 41, 63, and 65.

AMMONIUM MOLYBDATE METHOD.—*Kedesdy* * uses a nitric acid solution of ammonium molybdate for the comparison. The residue obtained in the extraction of the ink with ethyl acetate (*infra*) is dissolved in 100 c.c. of water; 1 to 2 c.c. of the liquid diluted to 25 c.c. and 5 c.c. of *Finkener's* molybdate reagent added. The yellow to brown coloration is matched against a standard solution of gallotannic and gallic acids, prepared by extracting *Schluttig* and *Neumann's* standard ink (p. 159) with ethyl acetate, drying the residue from the extract, and dissolving it in water.

The molybdate reagent is prepared by dissolving 80 grms. of ammonium molybdate in 640 c.c. of water and 160 c.c. of ammonia solution (sp. gr. 0·925), and cautiously adding to the solution a cold mixture of 960 c.c. of nitric acid (sp. gr. 1·18) and 240 c.c. of water.

OSMIUM TETROXIDE METHOD.—*Mitchell* † has shown that osmium tetroxide (the osmic acid of the microscopists) can be used as a sensitive reagent for tannins and their derivatives, being capable of detecting, *e.g.*, 1 part of gallic acid in 3,000,000. The coloration ranges from red-violet in dilute solutions to violet-black in con-

* *Mitt. Kgl. Materialsprüfungsamt*, 1907, xxv., 268.
† *Analyst*, 1924, xlix., 162.

centrated solutions. Unlike his ferrous tartrate reagent (*supra*), osmium tetroxide gives similar colorations with both the pyrogallol and catechol tannins.

For quantitative work, the ordinary 1 per cent. microscopic stain is diluted with 10 parts of water, and a solution of 0·1 grm. of pure pyrogallol, catechol, or gallic acid is used as the standard. The colorations produced by catechol and pyrogallol are relatively proportional to their molecular weights, and the same relationship applies to the colorations given by protocatechuic acid and catechol, but gallic acid gives a relatively more intense coloration than pyrogallol.

The method affords a convenient means of estimating the pyrogallol and catechol tannins together, in terms of catechol, pyrogallol, or gallic acid, and it has been applied to the analysis of various products such as extracts of wood, commercial sawdust intended for curing fish, bacon, etc. It has also been found applicable to the colorimetric estimation of tannins in coffee, hops, etc.

EXTRACTION WITH ETHYL ACETATE.—A method of extracting both gallotannic and gallic acids by means of ethyl acetate has been devised by *Hinrichsen*,* and has been adopted for the official valuation of inks in the Prussian regulations.

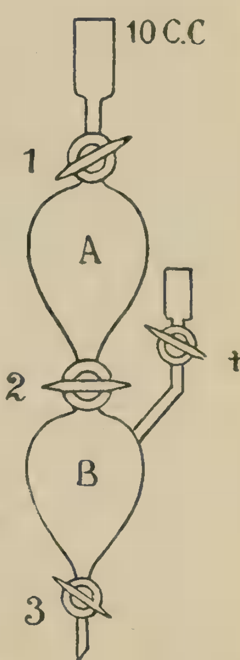


FIG. 35.—Rothe's extraction apparatus.

The ink (10 c.c.) is acidified with hydrochloric acid, and repeatedly shaken with the solvent, the united extracts evaporated *in vacuo*, and the residue weighed. The actual amounts of gallotannic and gallic acids in the residue may then be estimated by titration with iodine (see p. 169), or colorimetrically by means of ammonium molybdate (*supra*), or Mitchell's ferrous tartrate reagent (p. 97). For this purpose *Hinrichsen* recommends the use of *Rothe's* extraction apparatus (Fig. 35). Ten c.c. of the ink are introduced, by means of a pipette, into the bulb A, and 10 c.c. of concentrated hydrochloric acid into the funnel. After the introduction of the acid into A, 50 c.c. of ethyl acetate are added and the apparatus vigorously shaken and allowed to stand. The lower aqueous layer is then drawn off into the lower bulb, B, where it is shaken with a fresh portion of the solvent, which is introduced through the funnel, 4.

* *Collegium*, 1909, pp. 233, 242.

The new aqueous layer is withdrawn through the tap, 3, and, after removal of the extracts from A and B, it is returned to A, where the extraction is repeated with fresh supplies of the solvent. Finally the united extracts are evaporated and the residue treated as described on p. 169.

In this way *Hinrichsen* and *Kedesdy* found that the ethyl acetate extracts of galls consisted entirely of gallotannic and gallic acids, and that these acids constituted 60 to 80 per cent. of the extract from myrobalans and divi-divi.

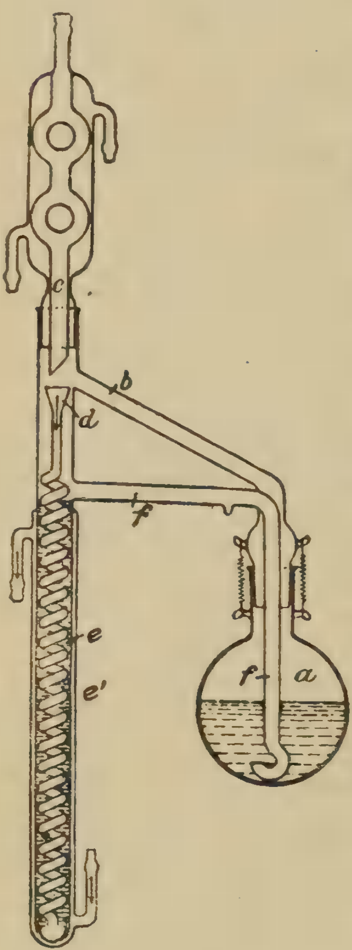


FIG. 36.—Kempf's apparatus for extracting tannin from ink.

It would therefore be impossible to detect the substitution of other tanning extracts (from which the portion insoluble in ethyl acetate had been removed) for galls in inks.

KEMPF'S APPARATUS.—The official method of estimating the amount of gallic and gallotannic acids in ink for classification by the Prussian regulations (*supra*) is tedious and open to the objection that, in hot weather, hydrolysis of the ethyl acetate may take place and the aniline dye or other provisional colouring matters in the ink be also extracted.

To obviate these drawbacks *Kempf* * has devised the automatic extraction apparatus shown in the accompanying diagram (Fig. 36). A mixture of 10 c.c. of the ink and 10 c.c. of 20 per cent. hydrochloric acid is introduced into the cylindrical vessel, *e*, which is surrounded by a cooling jacket, *e′*, and 100 c.c. of ethyl acetate are placed in the flask, *a*, the capacity of which is about 150 c.c. The solvent is kept briskly boiling, and the vapours rise through the tube, *b*, to the condenser, *c*, whence the condensed drops fall into the funnel, *d*, connected with the spiral tube standing loosely in the cylindrical vessel. Then, issuing from perforations in the expanded base of the spiral, the drops rise through the ink, and the extract overflows through the tube, *f*, into the flask, any trace of the ink carried over simultaneously being retained by the trap in the tube.

* *Mitt. Kgl. Materialsprüfungsamt*, 1913, xxi., 451.

Samples of the extract above the ink are tested at intervals to ascertain whether the extraction is complete. As a rule, the whole of the gallic and tannic acids is removed in about 1¼ hours, or about four times as rapidly as in the shaking method.

II. IRON SALTS.

Many iron salts could be used as the iron equivalent of iron-gall inks, but ferrous sulphate has long been regarded as practically the most suitable for the purpose. Ferric chloride, however, is used to a limited extent, and, of recent years, attempts have been made to make use of other iron salts.

FERROUS SULPHATE OR COPPERAS.—This is the salt to which reference is constantly made by Gebir (about 800 A.D.) and other alchemists as *vitriol of Mars*, or *green vitriol*, other vitriols, such as *blue vitriol* (copper sulphate or nitrate) and *white vitriol* (silver nitrate and, later, zinc sulphate), being made by dissolving the respective metals in vitriolic acid (sulphuric acid) or spirits of nitre (nitric acid).

The other old name for this salt, *Copperas*, is still commonly used in the ink industry. Contrary to what its name suggests, it has nothing to do with copper, but is derived from an old French word *Couperose*, to which was added the adjective *verte bleue* or *blanche*, according to which metal had been disintegrated (*couper*) by the action of acid.

Manufacture.—Ferrous sulphate is formed when iron is dissolved in sulphuric acid, hydrogen being liberated in the reaction. The usual method of preparing the salt, however, is by oxidising iron pyrites or schists containing pyrites. The mineral is first roasted to convert the disulphide, FeS_2, into the monosulphide, FeS. On exposure to moist air this compound absorbs oxygen and is converted into ferrous sulphate and free sulphuric acid. The mass is next extracted with water, and the resulting solution transferred to wooden vats, in which iron turnings have been placed to convert the small amount of free sulphuric acid present into iron sulphate.

Here it is concentrated by evaporation in the presence of metallic iron, and is afterwards drawn off from the yellow deposit, which consists mainly of calcium sulphate and basic iron sulphate, and is left to crystallise.

Another industrial process consists in mixing burnt iron pyrites with hot sulphuric acid, dissolving the paste in water, and reducing the ferric sulphate to ferrous sulphate by means of iron filings, after

which the solution is concentrated in the presence of metallic iron and crystallised.

The crystals formed at the ordinary temperature are bluish-green oblique rhombic prisms which contain 7 molecules of water, $FeSO_4 . 7H_2O$ (see Fig. 37). If crystallised at a high temperature (80° C.), the crystals contain only 4 molecules of water, and it is also possible to prepare them with two or with three molecules. The normal salt, with 7 molecules of water, theoretically contains 20·08 per cent. of iron, and the presence of iron in excess of this amount in a salt free from efflorescence is probably due to crystallisation at a higher temperature.

FIG. 37.—Crystals of copperas (natural size).

Properties.—Ferrous sulphate ($FeSO_4 . 7H_2O$) dissolves in about twice its weight of water at 15° C. At 90° C. water (100 parts) dissolves 370 parts of the crystals, but considerably less at 100° C. (333 parts).

The commercial product (copperas) varies in colour from a bluish-green or whitish-green to a bright grass green, which last colour is attributed to the presence of traces of ferric sulphate.

On exposure to the air the salt partially absorbs oxygen and becomes coated with a white layer which soon changes to yellowish-brown, owing to the formation of basic ferric sulphate.

$$3FeSO_4 + O + H_2O = Fe_2(SO_4)_3 . Fe(OH)_2.$$

In this condition it is technically known as *rusty*, and is usually regarded by ink manufacturers as of more value, probably owing to its accelerating the preliminary darkening of the ink in the vats.

Fourteen commercial samples of copperas examined by the writer during the last four years have contained a proportion of iron ranging from 18·14 to 25·92 per cent. In nearly every instance the manufacturer's price was proportional to the amount of iron, and practical tests showed that an ink prepared from copperas containing 18·77 per cent. contained too little iron when the calculation had been based upon the use of copperas containing the theoretical 20 per cent.

Acidity.—The commercial salt almost invariably has a slight acid reaction. For example, five of the above-mentioned samples showed an acidity (in terms of *N*-alkali solution) ranging from 0·11 to 0·37 c.c. per 1 grm.

Obviously this acidity increases the amount of strong acid in the final ink, and accounts for the presence of such acids in inks to which no mineral acid has been added as such.

In estimating the acidity of copperas the ordinary indicators, such as litmus or phenolphthalein, are not of much use, since, unless added in very large quantity, they are bleached. Better results are obtained by titrating the solution without any indicator, the end-point being shown by the liquid turning bluish-green as soon as the precipitation of ferrous hydroxide begins. The use of methyl red as indicator gives satisfactory results, but *Houben's* method * of using ferrous sulphide as an indicator, in the manner described above, does not give sharp results.

Another way in which the ferrous sulphate may influence the acidity of the ink is through the formation of a basic salt; such copperas may show pronounced acidity, and yet still neutralise added acid, so that an ink made from "rusty" copperas may show a different acidity from one prepared from the fresh green salt.

Double Iron Sulphates.—Double salts, containing alkali metals or ammonia in addition to iron, are obtained in crystals somewhat resembling copperas in appearance, but usually of a paler colour. The ammonium salt, ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, does not readily undergo oxidation on exposure to moist air. As it could be obtained without much difficulty in large quantities, it would probably be a useful substitute for copperas, especially for the preparation of "acid-free" inks.

* *Ber.*, 1910, lii. (B), 1623.

FERRIC CHLORIDE, Fe_2Cl_6, is prepared in the anhydrous state by passing dry chlorine over metallic iron heated to redness. It rapidly absorbs moisture from the air, and is readily soluble in water, alcohol, and moist ether.

In the hydrated condition it is prepared by dissolving hydrated ferric oxide in hydrochloric acid and crystallising the solution, when crystals containing 6 molecules of water ($Fe_2Cl_6 . 6H_2O$) are obtained. It also forms crystals containing 10 or 2 molecules of water.

Another method of preparing it in the hydrated condition is to pass chlorine through a solution of ferrous chloride and afterwards to evaporate the liquid.

In the anhydrous condition it is bright green in colour, but the hydrated salts are of a yellowish-brown colour. Determinations of its density at different temperatures have indicated that its formula at 400° C. may be represented as Fe_2Cl_6, whilst at 1,000° C. it corresponds to $FeCl_3$.

Ferric chloride, like ferrous sulphate, forms numerous double salts, such as, for example, ammonium ferric chloride.

An account of the ferri-gallates, prepared by *Silbermann* and *Ozorovitz* from gallic acid and ferric chloride, is given on p. 87.

FERRIC SULPHATE CHLORIDE.—This new double salt has recently been discovered and patented by Röhm.* It has a composition corresponding with the formula $FeSO_4Cl . 6H_2O$. It is remarkably stable, and is not hygroscopic or deliquescent. The great advantages claimed for its use in the manufacture of ink are that it does not, like ordinary ferric salts, act upon aniline dyestuffs, changing their colour, and that, unlike ferrous salts, it does not throw down a deposit when oxalic acid is used as the acid to render the ink stable.

PROPORTION OF IRON IN TECHNICAL PREPARATIONS.—According to *Walther*,† the iron salts and solutions commonly used in Germany for the manufacture of ink contain the following proportions of iron :—Ferrous sulphate, about 20 per cent. ; anhydrous ferrous sulphate, about 33·3 per cent. ; ferric chloride solution (technical), about 15 per cent. ; ferric chloride solution (sp. gr., 1·28), 10 per cent. ; crystalline ferric chloride, about 20 per cent. ; anhydrous ferric sulphate, about 25 per cent. ; and ferric sulphate solution, about 10 per cent.

* *Chem. Zeit.*, 1921, xlv., 842.

† *Chem. Zeit.*, 1921, xlv., 430.

CHAPTER IV.

MANUFACTURE OF IRON GALL INK.

CONTENTS.—The relative proportion of galls and ferrous sulphate—Deductions from the composition of ink deposits—**Old type of iron gall ink**—Old formulæ of iron gall inks—**Unoxidised iron gall inks—Gallic acid inks—Japan inks—Rapidly drying inks.**

THE process of preparing ink from Chinese or Aleppo galls is a very simple one. In Continental works the galls are crushed, mixed with straw, and treated with hot (not boiling) water in a high narrow oak vat which has a false bottom. The liquid percolates through small holes in this, its passage being assisted by the presence of the straw, and is then drawn off through a cock and pumped over the goods again and again until the whole of the tannin has been extracted.

The final extract, which should contain from 5 to 6 per cent. of tannin (*Viedt*), is then mixed with a solution containing the necessary amount of ferrous sulphate.

In this country the extraction is frequently not as complete as in the process described. The crushed, not powdered, galls are extracted with cold water, and sometimes a considerable amount of tannin is left in the insoluble residue, although it is claimed that the tannin extract is purer and much less liable to form deposits than when the whole of the soluble substances in the galls are extracted.

THE RELATIVE PROPORTION OF GALLS AND FERROUS SULPHATE.

HISTORICAL OPINIONS.—If we compare the numerous formulæ given by different chemists who have investigated the subject, it will be observed that there is frequently a great difference of opinion.

One of the earliest published formulæ is that given in 1660 by *Canneparius*,* in which 3 parts of galls are to be used to 1 part of ferrous sulphate.

* *De Atramentis.*

Lewis,* who made experiments with varying quantities in 1748, found that equal parts of galls and ferrous sulphate yielded a good black ink, but that the colour faded in a few days to brownish-yellow on exposing the writing to the light. An infusion from 2 parts of galls mixed with 1 part of ferrous sulphate had not faded so much after two months' exposure, and with a proportion of 3 to 1 the colour was preserved still better. By still further increasing the proportion of galls to 6 : 1, the writing was paler but more durable. The proportion of water was found to admit of much greater variation, but 40 to 50 parts yielded an ink of sufficient blackness and permanence.

Riteaucourt † confirmed *Lewis's* statement as to the influence of an excess of iron upon the writing, and also showed that when the galls were in excess the characters soon changed to brownish-yellow on exposure.

From his experiments he concluded that a proportion of 2 of galls to 1 of ferrous sulphate was sufficient to make a good ink, and that *Lewis's* proportion of 3 to 1 was too great.

Other proportions recommended are 4 : 1 (*Eisler*,‡ 1,770) : 5 : 1 (*Reid* §) : 1·5 : 1 (*Brande* ||) ; 2·4 : 1 (*Ure* ¶) ; etc., etc.

All these proportions were obtained, empirically, with galls which probably contained very variable proportions of gallotannin, and by methods in which different amounts of that substance were brought into solution. But, making allowance for this, the balance of opinion, which is also supported by numerous authorities not quoted above (*Booth*, *Karmarsch*, *Hochheimer*, etc.), is in favour of a proportion of 3 parts or thereabouts of galls to 1 part of ferrous sulphate.

This conclusion is supported by the experiments of *Schluttig* and *Neumann* on the composition of the insoluble iron compound that forms on exposing the solution of gallotannic acid and ferrous sulphate to the action of the air, and by Mitchell's experiments on similar lines.

DEDUCTIONS FROM THE COMPOSITION OF INK DEPOSITS. —Of the numerous compounds of tannin and iron, which have already been described (p. 85), those formed during the spontaneous oxidation of the ink are the only ones that need be considered here, for the insoluble tannate produced by oxidation with hydrogen peroxide has a completely different composition (*loc. cit.*, *supra*).

* *Loc. cit.*, p. 377.
† *Ann. de Chim.*, 1792, xv., 113.
‡ *Loc. cit.*
§ *Phil. Mag.*, 1827, ii., 114.
|| *Dict. of Science*, art. Ink.
¶ *Dict. of Chem.*

*Wittstein** exposed a solution of tannin and ferrous sulphate in the proportion of 3 : 1 to the atmosphere for a month and a half, and thus obtained an insoluble precipitate which, when dried at 100° C., yielded 8·40 per cent. of ferric oxide (= 5·88 per cent. of iron). He proved that gallic acid was not formed in the oxidation, since the liquid, after repeated treatment with gelatin to remove tannic acid, yielded a filtrate which did not darken on the addition of ferric salts. The precipitate contained $\frac{1}{48}$ of its iron in the ferrous state.

The formula which best corresponds with this proportion of iron is that suggested by *Schiff*,† which requires 8·5 per cent. of iron oxide :—

$$\begin{array}{l} Fe \diagdown \; (C_{14}H_9O_9)_5 \\ \qquad > C_{14}H_8O_9 \\ Fe \diagup \; (C_{14}H_9O_9)_5 \end{array}$$

Schluttig and *Neumann*,‡ on repeating *Wittstein's* experiments, obtained a series of five spontaneous precipitates which they removed from the ink from time to time, the final one being collected after an exposure of five weeks. These five precipitates, dried at 100° C., were found to contain from 6·27 to 6·61 per cent. of iron, the average of the five being 6·35 per cent.

Precipitates obtained in the same manner and allowed to dry spontaneously in the air contained on the average 4·8 per cent. of iron. A complete analysis of one of these air-dried deposits gave the following results :—Carbon, 35·77 ; hydrogen, 5·19 ; iron, 4·80 ; and oxygen, 54·24 per cent. When these precipitates were dried at 100° C., the dark violet colour changed to black, and they were then found to contain 6·34 per cent. of iron, or the same proportions as the deposits dried directly at that temperature.

The ratio of iron to tannin was thus as 1 : 14·27 (or 1 part of ferrous sulphate to 2·88 parts of tannin)—a result which agreed fairly well with *Dieterich's* empirical proportion of 1 part of iron to 15 parts of tannin.

As there was considerable discrepancy between the composition of the deposits obtained by *Wittstein* and by *Schluttig* and *Neumann*, the writer thought it advisable to repeat once more the work, using not only tannins, but also extracts of different kinds of galls, etc.

The results, which, as will be seen, were obtained under very varying conditions, are summarised in the preceding table.

* *Jahresber. der Chem.* (von Berzelius), 1848, xxviii., 221.
† *Ann. Chem. Pharm.*, 1875, clxxv., 176.
‡ *Die Eisengallustinten*, Dresden, 1890, p. 44.

Amount of Iron in Spontaneous Deposits from Inks.

No.	Tannin, &c.	Ferrous sulphate.	Water.	Time before collecting the deposit.	Ferric oxide in deposit.	Iron in deposit.
		Grms.	C.c.		°/₀	°/₀
1	Gallotannic acid (86 °/₀) (2 grms.)	3	100	1 month	8.22	5.75
2	" " "	"	"	3 days.	8.49	5.94
1	Gallotannic acid (86 °/₀) (3 grms.)	3	100	1 week	7.85	5.49
2	" " "	"	"	"	8.63	6.04
1	Gallic acid (3 grms.) (very slight deposit)	2	250	2 months	25	17.5
1	Chinese galls, decoction from 12 grms.	3	200	10 days	9 8	6.8
2	" " " "	"	"	7 "	10.3	7.2
3	" " " "	"	"	3 weeks	10.8	7.55
4	" " " "	"	"	2 "	10.81	7.56
1	Aleppo blue galls, decoction from 5 grms.	1	200	4 days	8.62	6.04
2	" " " "	"	"	10 "	11.03	7.72
3	" " " "	"	"	3 weeks	10.6	7.4
1	English oak-apple galls, from 5 grms.	1	200	2 weeks	14.8	10.3
2	" " " "	"	"	1 week	12 9	9.0
3	" " " "	"	"	1 "	13.1	9.2
1	Japanese galls (5 grms.)	1	200	6 days	11.31	7 91
2	" " "	"	"	3 weeks	11.02	7.71
3	" " "	"	"	6 days	11.6	8.12
1	Divi-divi (5 grms.)	1	200	2 weeks	9.70	6.77
2	Ink decanted from first sediment	"	"	" "	11.11	7.77
1	Valonia (5 grms.)	1	200	1 week	11.53	8.1
2	" "	"	"	2 weeks	12 78	8.9
1	Myrobalans (5 grms.)	1	200	2 weeks	8.21	5 74
1	Chestnut extract (5 grms.)	5	200	1 month	10.53	7.37

Other results, indicating the probable nature of the changes which occur during the drying of ink, are given on p. 88.

The results with pure gallotannic acid are thus more in agreement with those of *Wittstein* than with those of *Schluttig* and *Neumann.*

It was hardly to be expected that galls should not contain other substances, besides gallotannic acid, forming insoluble compounds with iron, and this probably accounts for the higher percentage of iron found in the deposits from English oak-marble gall ink, etc.

As the precipitates attacked the paper, if dried on the filter at 100° C., the deposits were washed into a platinum basin, in which they were subsequently dried and ignited.

The ratio between the iron and gallotannic acid in the dried deposits was as 1 : 16, which corresponds with a ratio of 1 : 3·22 between the ferrous sulphate and gallotannic acid.

Hence, each part of ferrous sulphate requires 3 parts of pure gallotannic acid. Since, however, the proportion of tannic acid varies in each kind of material employed, the proportion of tannin material must naturally vary correspondingly.

The following table, giving the approximate proportions of different materials, is based upon the average amount of tannins they contain, and on the results of the preceding experiments. It is assumed that practically the whole of the tannin is extracted in each case.

Proportion of Tannin Materials required by 1 *part of Ferrous Sulphate.*

Tannin material.	Containing pure tannic acid.	Parts by weight required.
	Per cent. (*circa*).	
Commercial gallotannic acid . .	86	3.8
Aleppo galls.	62	5.0
Chinese galls	75	4.3
Japanese galls	62	5.0
Acorn galls (Knoppern) . . .	30	11
English oak-apple galls . . .	26	12.5
Chestnut wood	9	36
,, ,, extract	20	16
Sumach	22	14.6
Valonia*	30	11
Divi-divi	40	8
Myrobalans	30	11

* See also colorimetric results on p. 67.

Old Type of Iron Gall Inks.

When solutions of gallotannic acid and ferrous sulphate are mixed the liquid at first remains colourless, and it is only when oxidation takes place that a violet-black solution, and eventually a violet-black deposit, is formed.

In the older type of iron gall inks it was, therefore, necessary to expose the liquid to the air for some time to obtain an ink which would give writing of sufficient immediate blackness, although even the writing with the colourless solution of gallotannic acid and ferrous sulphate gradually becomes black when dried. In other words, a "provisional colour" was formed by partial oxidation of the ink, and the colloidal or insoluble deposit was kept in suspension by the addition of a sufficient quantity of gum arabic.

Ink thus oxidised yielded an immediate black writing, but had the drawback that that portion of the ink in which the oxidation was complete did not penetrate into the fibres of the paper, but was attached to the surface by means of the gum and could be washed off.

In a good iron gall ink of the old type it was, therefore, essential to have only so much of the ink oxidised as to give a black colour at once, leaving the remainder in an unoxidised state to penetrate into the paper, and form the black insoluble oxidised tannate within the fibres.

On boiling an iron gall ink the oxidation process is accelerated, and there is also some decomposition of the tannate, so that a complete ink should not be boiled.

Provisional Colouring Matters.—The paleness of the writing with unoxidised ink has also been obviated in many inks by the addition of logwood extract (p. 123), or more recently of various aniline colours (p. 118). Such colouring matters as Prussian or Turnbull's blue, ultramarine, or the various blue compounds of copper, are quite unsuitable for the purpose, since they are either too insoluble or react with the tannin and affect the colour of iron tannate. Formerly the most widely employed substance as a provisional colour was indigo, the presence of which is a characteristic feature of the so-called "*alizarine*" *inks* (*vide infra*).

OLD FORMULÆ OF IRON GALL INKS.—The earliest method of preparing iron gall ink that we have discovered is that of the Elizabethan domestic ink, the formula of which is shown in the frontispiece.

Elizabethan Ink.—Rain water (or claret wine or red vinegar), 1 quart; galls, 5 ozs.; ferrous sulphate, 4 ozs.; gum, 3 ozs. After

five days' soaking, the extract from the galls was heated just to the boiling point with the ferrous sulphate (see also the rhyme of *de Beau Chesne*, p. 12).

Canneparius * (1660).—Galls, 3 ozs., macerated in 30 ozs. of white wine for six days, and the extract mixed with 1 oz. of ferrous sulphate and 2 ozs. of gum arabic, and left for four days.

Lewis † (1760).—Galls, 3 ozs.; rasped logwood, 1 oz.; water, 2 to 3 parts; gum, varied at discretion, but about ½ oz. per pint. The ink to be shaken daily for ten to twelve days.

"*Celebrated Black Dresden Ink*" (1770).‡—Galls, 2 lbs.; ferrous sulphate, ½ lb.; gum, 6 ozs.; alum, 2 ozs.; verdigris, 1 oz.; and salt, 1 oz.; in 2 quarts of vinegar and 2 quarts of rain water. Decanted after two days and shaken daily for eight days.

Eisler ‡ (1770).—Galls, 4 ozs.; ferrous sulphate, 2 ozs.; gum, 1 oz.; in a quart of rain water.

Ribeaucourt § (1792).—Galls, 2 ozs.; ferrous sulphate, 1 oz.; copper sulphate, ¼ oz.; gum, 1 oz.; and logwood, 1 oz.; in 24 ozs. of water.

Reid || (1827).—Galls (1 lb.) extracted twice with 3 pints of boiling water, and the extract (2 quarts) mixed with $3\frac{1}{7}$ ozs. of ferrous sulphate and the same quantity of gum.

Unoxidised Iron Gall Inks.

The use of indigo as a means of improving the colour of ink was mentioned by *Eisler* in 1770 (*loc. cit.*), and was used in this country by *Stephens* ¶ in 1836.

In 1856 *Leonhardi*,** of Dresden, patented in Hanover an ink consisting of an extract of 42 parts of Aleppo galls and 3 parts of madder in 120 parts of water, mixed with $1\frac{1}{5}$ parts of indigo solution, 5 parts of ferrous sulphate, and 2 parts of metallic iron, dissolved in crude acetic acid. Subsequently the madder was omitted as superfluous, but the inks still retained the name of "alizarine" ink, although quite free from alizarine. The more suitable name of "*isatin*" inks never met with popular acceptance.

In "alizarine" inks the process of oxidation is prevented as far as possible, thus keeping the liquid free, to a large extent, from insoluble deposit, and giving it much greater power of penetration into the paper. The presence of the indigo makes the writing

* *De Atramentis*, p. 270.
† *Loc. cit.*, p. 377.
‡ Eisler, *Dintefass*, p. 7.
§ *Ann. de Chim.*, 1792, xv., 113.
|| *Philos. Mag.*, 1827, ii., 114.
¶ *Mechanics' Mag.*, 1836, xxv., 229.
** *Dingler's polyt. Journ.*, 1856, cxlii., 141.

immediately blue, and it subsequently changes to black as the oxidation of the iron tannate proceeds within the fibres of the paper.

The addition of indigo also increases the permanence of the ink, so that the writing offers much more resistance to the action of bleaching agents than ordinary iron gall inks.

Owing to the absence of gum, the inks flow more readily from the pen, and are less liable to clog ; but, on the other hand, the presence of free acid in considerable proportion causes the pen to be corroded somewhat rapidly.

Thus we found that an ordinary steel pen left in a typical commercial "alizarine" ink from which air was excluded had lost 5 per cent. in weight after six weeks, while the ink itself had become semi-solid (see p. 162).

Indigo blue is soluble in concentrated sulphuric acid, and the solution can be diluted to a great extent without yielding a deposit.

Viedt * gives the following method of preparing "alizarine" ink :—A 5 to 6 per cent. solution of sulphindigotic acid is treated with sufficient iron to form the necessary amount of ferrous sulphate for the tannin present. The excess of free acid is then nearly neutralised with chalk or marble, only a slight amount being left to retard atmospheric oxidation of the ink. The clear solution is decanted from the insoluble calcium sulphate and mixed with a 5 to 6 per cent. decoction of galls, a green solution being thus obtained through the mixture of the yellow gall extract and blue indigo solution.

Inks containing neutral indigo carmine—*i.e.*, the sodium or potassium salt of sulphindigotic acid—yield deposits much more readily than inks containing free sulphuric acid, though the latter also form sediments in time.

Indigo carmine is prepared by dissolving indigo in sulphuric acid, adding alkali, and collecting and washing the precipitate.

Prollius' "Alizarine" Ink, which was recommended by *Bley* † as superior to any then sold, was prepared from (1) 1¼ lbs. of galls, with sufficient water to yield 5 lbs. of decoction ; (2) 4 ozs. of indigo powder mixed with 1⅓ lbs. of fuming sulphuric acid, and allowed to stand for 24 hours ; then diluted with 5 lbs. of water, treated with 8 ozs. of powdered chalk, and 8 ozs. of iron filings, filtered and added to (1).

With the object of reducing the corrosive action of the sulphuric acid in the ferrous sulphate upon steel pens several manufacturers have proposed to ignite ferrous sulphate until a white powder was left. It is difficult to see what advantage such a process can have.

* *Ibid.*, 1875, ccxvi., 533. † *Dingler's polyt. Journ.*, 1857, cxlv., 77.

Desormaix's gall ink * *and Hänle's non-corrosive ink* † were prepared in a similar manner.

Gallic Acid Inks.

Reid,‡ in the course of his investigation on gall inks, pointed out that after the conversion of gallotannic acid into gallic acid more than twice as much ink was produced. Thus 448 parts of galls required 144 parts of ferrous sulphate, but after the conversion of the gallotannic acid into gallic acid 336 parts of the iron salts were necessary to obtain an ink of the same intensity (*cf*. p. 77).

To effect this conversion in practice, he exposed a decoction of 1 lb. of galls to the air for ten days with continual daily shaking, and then added to each quart of the liquid $3\frac{1}{2}$ pints of water, 9 ozs. of ferrous sulphate, and 9 ozs. of gum.

Dieterich § has also recommended inks prepared from gallic acid solutions obtained by the oxidation of gall extracts or tannin solutions.

Oxidised Gall Extracts.—200 parts of powdered Chinese galls are moistened with water and kept in a warm place (20° to 25° C.) until quite mouldy, the water being renewed daily, so that the galls feel moist but not wet. After eight to ten days the fermentation is complete, and the galls are extracted with successive portions of hot water, and filtered after the addition of some talc, the total amount of extract and washings amounting to 1,000 parts.

Oxidised Tannin Solutions.—100 parts of tannin, 100 parts of water, and 20 parts of hydrochloric acid (sp. gr. 1·16) are heated for ten hours on the water-bath at 80° to 90° C., and then gradually diluted with 900 parts of distilled water.

For writing inks *Dieterich* finds that either ferrous or ferric salts can be used with such oxidised solutions, but for copying inks only ferrous salts can be employed (see Chap. xii.). He gives the following directions for preparing inks on these lines :—

I. *Gall Ink*.—1,000 parts of the oxidised gall decoction are mixed with 100 of ferric chloride solution containing 10 per cent. of iron the ink left for two weeks in closed flasks and then decanted.

II. *Oxidised Tannin Office Ink*.—100 parts of tannin, 100 of water, 200 of ferric chloride solution (10 per cent. of iron), and 10 per cent. of crude hydrochloric acid (sp. gr. 1·16) are mixed and heated for ten hours at 80° to 90° C. The liquid is then diluted with 700 parts of hot water, left for an hour at the same temperature (with renewal of

* *Nicholson's Dict. of Chem.*, 1820, p. 507.
† *Prechtl's Technol. Encyclop.*, 1852, p. 460.
‡ *Philosoph. Mag.*, 1827, ii., 111.
§ *Pharm. Manual*, 1897, p. 680.

the evaporated water), cooled, kept in a closed flask for two weeks, filtered and diluted to 1,000 parts.

With inks thus prepared the writing is at first hardly perceptible, so that a provisional colour is necessary, as in the case of the following formulæ :—

Blue-black Iron Gall Ink.—Three parts of phenol blue in 400 parts of water are mixed with 600 parts of oxidised gall ink (I.) and 1 part of phenol, and left for a week in a loosely covered flask, after which the clear ink is decanted.

Violet-black Ink.—Prepared in the same way, except that 1·5 parts of phenol blue 3 F, and 2·0 parts of Ponceau red RR are used, instead of the three parts of phenol blue as the provision colour.

Red-black Ink.—Six parts of Ponceau red R used.

Green-black Ink.—Six parts of aniline green used.

Black Ink.—The provisional colour consists of 10·5 parts of aniline green D, 9 parts of Ponceau red R, and 1 part of phenol blue 3 F.

"*Alizarine*" *Ink.*—Four parts of indigotin, and 2·4 parts of aniline green as colouring matter.

Blue-green Ink.—1·5 parts of phenol blue, and 2·5 parts of aniline green as colouring matter.

For the formulæ of gallic acid copying inks on these lines see Chap. xii.

State of Massachusetts Official Ink.—This is a mixed tannic and gallic acid ink, containing the following constituents : Dry gallotannic acid, 23·4 ; gallic acid crystals, 7·7 ; ferrous sulphate, 30 ; gum arabic, 25 ; dilute hydrochloric acid, 25 ; and phenol, 1, in 1000 parts of water.

Standard German Inks.— According to *Walther* * five classes of inks are made by German ink-makers, and two of them are officially recognised by the *Materialprüfungsamt.* For the preparation of these he recommends the use of ferric chloride solution (sp. gr. 1·28) with hydrochloric acid (20° to 22° Bé.) as the acid :—

Class, . .	0	1	2	3	4
Tannin (80 per cent.), .	28	19	15	12	10
Gallic acid, ...	7	5	3	3	2
Ferric chloride solution,	30	20	15	12	10
Hydrochloric acid, .	8	8	8	7	7
Aniline dye, . . .	3 to 6	3 to 6	3 to 6	3 to 6	6 to 6
Phenol, ...	1	1	1	1	1
Water, ...	1,000	1,000	1,000	1,000	1,000

* *Chem. Zeit.*, 1921, xlv., 430.

The tannin, gallic acid and aniline dye are dissolved in 200 litres of boiling water, and the iron chloride solution is diluted with 200 litres of cold water, and the two solutions are mixed. The acid is then added, and the whole diluted with 600 litres of water and the phenol added. Gum may be added when a paper poorly sized is used; otherwise it is unecessary.

Japan Inks.

When an iron gall ink has been oxidised so as to have become converted for the most part into colloidal or insoluble black iron tannates (p. 114), it no longer possesses the penetrating properties of the freshly prepared ink, and requires the addition of a considerable amount of gum to keep the insoluble powder in suspension.

Such ink immediately gives black writing, which dries on the surface of the paper with a varnish like gloss, whence this sort of ink was termed *Japan ink* by *Ribeaucourt.*

Since the oxidation has taken place within the ink instead of partly within the fibres, as in the old type of partially oxidised gall inks, Japan inks are more easily removed than other gall inks. They have also the drawbacks of stickiness and that the excess of gum clogging the pen, and, at the same time, they also readily yield large deposits.

Ribeaucourt's Japan Ink contained the ingredients given in the formula on p. 115. In *Newton's* English patent (No. 836; 1865), complete iron gall ink was oxidised by being percolated through narrow openings in the bottom of a vessel; whilst *Carter* (Eng. Pat., No. 1982; 1873) obtained the same results by subjecting the ink to the action of a current of air.

Both of these processes produce "Japan" inks of the very opposite type to "alizarine" inks.

Rapidly Drying Inks.

Inks that are intended to dry immediately after writing contain as an essential ingredient a considerable proportion of a volatile liquid. For example, *Rüler* has patented in France (1909) the use of spirits of wine, in the proportion of 1 part in 5, as an addition to the ink. The same principle is used for stamping inks (Chap. xvi.).

CHAPTER V.

LOGWOOD, VANADIUM, AND ANILINE BLACK INKS.

CONTENTS.—**Logwood inks**—Logwood—Logwood extract—Hæmatoxylin—Hæmatein—Iso-hæmatein—Addition of logwood to gall inks—Logwood inks without tannin—Chrome logwood inks—Hæmatein inks—Use of logwood in patent inks—**Vanadium inks**—**Black aniline inks.**

LOGWOOD INKS.

LOGWOOD.—This well-known dyeing material consists of chips of the wood of *Hæmatoxylon Campechianum*, a large tree (40 to 50 feet high) belonging to the *Cæsalpiniaceæ*. It forms large woods on the Atlantic side of Central America, in Mexico, and in the West Indies.

It was first discovered by the Spaniards in the Bay of Campeachy, in Mexico, and exported by them into Europe. When introduced into England in the reign of Queen Elizabeth, it was soon employed to adulterate other dyes, and its use was prohibited as "affording a false and deceitful colour" injurious to the Queen's subjects, "and discreditable beyond seas to our merchants and dyers." This Act was not repealed until 1661.

The constant hostilities between the Spanish and English led to the acclimatisation of the tree in the West Indies in 1715, though subsequently a treaty was concluded giving the English the right of cutting and exporting the wood from Campeachy.

The West Indian logwood is not so valuable as the Mexican product, whilst Honduras wood is intermediate in value.

In preparing it for the market, the wood is first divided into logs about 3 feet in length, which are then cut into chips by means of a revolving drum provided with steel cutting knives.

LOGWOOD EXTRACT.—Formerly the chips were moistened and exposed to a fermentation process, but manufacturers now endeavour to exclude all oxidising influences.

Three methods are in use in the preparation of the logwood extracts of commerce.* The finely divided chips are frequently digested with hot water under a pressure of 1 to 2 atmospheres, this

* Rupe, *Die Chem. der natur. Farbstoffe*, p. 107.

process yielding a large extract, which, however, contains a considerable proportion of resins, oil, and other impurities; (2) the French method of boiling the chips with water at the ordinary pressure, which yields a smaller though purer extract; and (3) a diffusion process, in which an apparatus similar to that used in the sugar industry is employed. The yield by this process is smaller than in (1) or (2), but the shades of colour are finer.

If the wood has not undergone any fermentation, the extracts contain chiefly hæmatoxylin and but little hæmatein. They are sold either as liquids, with a density of about 10° Bé., or as solid gum-like masses.

The tinctorial value of an extract is usually determined by practical dyeing tests, the amount of colour fixed on wool mordanted with potassium dichromate and tartaric acid, on treatment with a definite quantity of the dried sample, being compared with that given by a sample of standard quality.

Logwood extract may be adulterated with molasses or tannin materials, though according to *Rupe* (*loc. cit.*) adulteration is not so frequent now as formerly.

HÆMATOXYLIN ($C_{16}H_{14}O_6$).—The colouring matter of logwood does not occur ready formed in the cells, but in the form of a compound, *hæmatoxylin*, which becomes purple on oxidation.

Hæmatoxylin was first discovered by *Chevreul** in 1810, and termed *hæmatin* by him, a name subsequently changed to *hæmatoxylin* by *Erdmann*,† in order to prevent confusion with the colouring matter of blood.

It was obtained by *Hesse* ‡ in the form of colourless crystals containing 3 molecules of water (which they lose at 120° C.), by extraction with ether containing some water and in the presence of alkali bisulphite.

Properties.—Hæmatoxylin has a sweet taste and is slightly soluble in water, but dissolves readily in alcohol and ether. The crystals turn red on exposure to the light (in the absence of air) without changing in composition.

Solutions of silver and gold salts are rapidly reduced by them, as is also the case with Fehling's solution. Stannous chloride gives a rose-coloured precipitate, ferrous ammonium sulphate a slight violet-black precipitate, and lead acetate a white precipitate changing to blue.

On dry distillation hæmatoxylin yields pyrogallol and resorcinol (or a derivative).

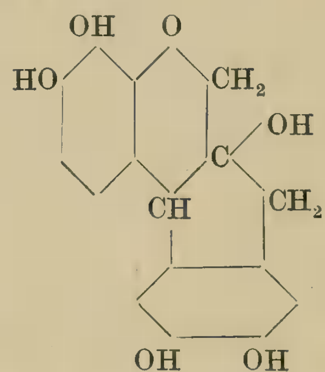
* *Ann. Chim. Phys.*, 1812, lxxxii., 53, 126.
† *Ann. Chem. Pharm.*, 1842, xliv., 292.
‡ *Ibid.*, 1859, cix., 332.

From a consideration of the results obtained on acetylation *Reim** concluded that hæmatoxylin had the constitutional formula,

$$\begin{array}{l} C_6H_2(OH)_3 \\ | \\ C_6H_4 \\ | \\ C_6H_2(OH)_3 \end{array}$$

which supported the views of *Schluttig* and *Neumann* (p. 83).

It has now been established, however (*W. H. Perkin*), that the following structural formula must be assigned to hæmatoxylin :—



This does not contain three adjacent hydroxyl groups, and hence does not agree with *Schluttig* and *Neumann's* theory.

HÆMATEIN ($C_{16}H_{12}O_6$).—The colouring principle of logwood, which is first formed by the oxidation of the pre-existing hæmatoxylin, was discovered by *O. Erdmann* (*loc. cit.*)—$C_{16}H_{14}O_6 + O = C_{16}H_{12}O_6 + H_2O$.

It forms small anhydrous yellowish-green crystals with a metallic lustre. These are only slightly soluble in water, alcohol, or ether, though the solution in water (0·06 per cent. at 20° C.) has an intense colour.

It is readily soluble in alkalis, yielding violet or purplish-brown compounds. The ammonium compound, $C_{16}H_{12}O_6 . 2NH_3$, is precipitated by most metallic salts. Thus it yields a violet-blue precipitate with copper sulphate, a dark violet with alum, and a black one with iron ammonium sulphate, whilst it reduces a solution of silver nitrate (*Hesse*).†

Hæmatein is reduced to hæmatoxylin by treatment with sulphur dioxide or hydrogen.

ISO-HÆMATEIN.—When hæmatein is treated with concentrated sulphuric acid, it dissolves, forming a brown solution, from

* *Ber.*, iv., 329. † *Loc. cit.*

which, on standing, a crystalline compound, $\left.\begin{matrix} C_{16}H_{11}O_5 \\ H \end{matrix}\right\} SO_4$, is deposited (*Hummel and Perkin*).*

If hydrochloric acid be heated with hæmatein in a sealed tube the colour of the solution changes to dirty yellow, and on evaporating the liquid a crystalline deposit of iso-hæmatein hydrochloride is left. By treating this with silver hydroxide, and concentrating the solution *in vacuo*, *iso-hœmatein* is left as an amorphous mass with greenish metallic lustre.

Iso-hæmatein has the same composition as hæmatein, which it also resembles in its general reactions, though many of the metallic compounds have a more reddish shade of purple.

ADDITION OF LOGWOOD TO GALL INKS.—The advantage of adding a small proportion of logwood decoction or extract to iron gall inks has long been known. In 1763 *Lewis* † made a series of experiments to determine whether such an addition had any injurious effect upon the stability of the ink, and found that the colour of the ink was materially improved without any reduction in permanency.

He recommended an ink consisting of 3 parts of galls, 1 of ferrous sulphate, and 1 of logwood in 40 to 60 parts of water, with gum arabic in the proportion of ½ part to 20 of ink.

Eisler's Logwood Gall Ink ‡ was prepared from the following ingredients :—Logwood, 8 ozs. ; ferrous sulphate, 8 ozs. ; vinegar, ½ quart ; rain water, ½ quart ; galls, 4 ozs. ; gum arabic, 4 ozs. ; alum, 2 ozs. ; and indigo, 1 oz. The ink was left for fourteen days in the sun before using.

Ribeaucourt § in 1792 agreed with *Lewis's* statement as to the advantage of logwood in iron gall ink, and recommended that its proportion should be half that of the galls.

These earlier results have been fully confirmed in our time by the experiments of *Schluttig* and *Neumann*,‖ who found that ink prepared from hæmatoxylin and iron was even more permanent than those prepared from gallotannic or gallic acids.

Reid's Gallic Acid Logwood Ink.—*Reid* ¶ found that when gallic acid was employed in place of gallotannin logwood might be added in the proportion of 1½ parts to 1 part of the former.

He prepared an ink on these lines by exposing a decoction of galls (1 lb.), to the air for ten days with occasional daily agitation, so as to convert the gallotannin into gallic acid, and then adding

* *Ber.*, xv., 2337.
† *Loc. cit.*, p. 377.
‡ *Dintefass*, 1770, p. 8.
§ *Ann. de Chim.*, 1792, xv., 113.
‖ *Die Eisengallustinten*, p. 33.
¶ *Philos. Mag.*, 1827, ii., 115.

a decoction of logwood (1½ lbs.), 18 ozs. of ferrous sulphate, and 18 ozs. of gum.

This ink is decomposed by alkalis and alkali carbonates, the iron being precipitated.

LOGWOOD INKS WITHOUT TANNIN.—The iron logwood inks have a greenish shade, which gradually changes to black as the writing dries. Alum logwood inks have a deep violet-black colour, and chromium logwood inks a violet colour changing to black. Chromic acid added to logwood gives a deep black precipitate, and potassium chromate yields a black ink, and if added in excess a black precipitate.

In fact, as *Viedt** has shown, precipitates are gradually formed by oxidation in logwood inks containing alum or iron or copper salts, though more slowly than in iron tannin ink. The addition of logwood in excess does not prevent this, but the deposition is retarded for a long time by completely excluding the air.

Reinige's Iron Logwood Ink.†—This may be taken as a typical ink of this class. It is prepared by dissolving 2 grms. of logwood extract, and 3 grms. of ferrous sulphate, in 100 c.c. of water, then adding 10 grms. of crystalline sodium carbonate, and finally, 2 grms. of oxallic acid. After complete settlement the ink is decanted from the sediment, and a suitable proportion of gum added.

This ink gives a good black writing, but we have found that the characters become somewhat brown after two or three months.

The writing gives a red coloration with hydrochloric and other acids, due to the logwood, and a bluish-green with acidified potassium ferrocyanide solution, indicating the iron. It is gradually bleached by bromine water.

Reid,‡ who investigated the character of the inks formed on adding ferrous sulphate to logwood, found that the greenish-blue compound first formed was gradually oxidised to a brownish-black compound. Copious deposits were given, however, by such logwood iron inks, and hence *Reid* concluded that logwood should not be employed alone, or should not exceed a third of the amount of the galls in mixed inks.

Böttger's Alum Copper Logwood Ink.§—This is prepared by boiling 1 part of alum, 2 of copper sulphate, and 4 of logwood extract with 48 parts of water, and filtering the solution. The filtrate is a red-violet ink, which writes pale violet, but rapidly darkens and soon becomes jet black.

* *Dingler's polyt. Journ.*, 1875, ccxvi., 456.
† *Ibid.*, 1857, cxliii., 240. ‡ *Philos. Mag.*, 1827, ii., 114.
§ *Dingler's polyt. Journ.*, 1857, cxliii., 240.

On treatment with bromine water the writing is changed to red, and then to faint brownish-yellow.

The great drawback of the ink is its instability, and it must be kept in tightly corked bottles, which should contain as little air as possible. Ink prepared by the writer and kept in a corked bottle containing air had yielded a dense deposit in six weeks, and gave only faint writing.

Violet-Black Rouen Ink (*Encre bleu rouennaise*).*—This consists of a decoction of 75 parts of logwood in 600 parts of water, to which is added 3½ parts of alum, 3 parts of gum arabic, and 1½ parts of sugar candy. The ink is allowed to stand for two or three days and then strained.

Inks containing only logwood and alum write with a reddish-violet colour, which gradually changes to a dark, though not absolutely black, shade.

Viedt's Copper Logwood Ink.†—In *Viedt's* opinion copper sulphate should always be used in preference to ferrous sulphate in logwood ink, since it gives a blacker writing.

He recommends the following formula:—Logwood extract, 20 kilos. in 200 kilos. of water, mixed with a solution of 10 kilos. of ammonium alum in 20 kilos. of boiling water, and the mixture treated with 0·2 of sulphuric acid and 1·5 of copper sulphate in 20 litres of water.

In order to obtain a darker liquid the ink is exposed to the air for some days before being bottled, thus producing a "provisional colouring," similar to that given by indigo in "alizarine" inks. Inks of this type are sold under different names—*e.g.*, *Chemnitz violet-black ink*.

To obviate the paleness of the writing with such inks as this *Stark* has prepared a writing and copying ink which gives immediate black characters by adding a little chromate to a copper logwood ink, the chrome ink in this case representing the "provisional colouring" matter (*cf.* p. 13).

Viedt (*loc. cit.*) states that he has never known an ink of this kind to gelatinise.

A great objection to all logwood copper inks is that they cannot be used with steel pens, for these gradually withdraw the copper from them.

The addition of free sulphuric acid, as in *Viedt's* copper logwood ink (*supra*), retards the formation of a deposit, but causes the ink to corrode steel pens.

* *Ibid.*, 1859, cliii., 77. † *Ibid.*, 1875, ccxvii., 76.

CHROME LOGWOOD INKS.—*Runge* * discovered that by adding a very small proportion of potassium chromate to a decoction of logwood a deep black fluid was obtained, which could be used at once as a writing ink, though by increasing the amount of chromate a black precipitate was produced.

Runge's Chrome Ink.—This was originally prepared by boiling 10 lbs. of logwood with water until 80 lbs. of decoction were obtained, and adding potassium chromate in the proportion of 1 part in 1,000.

If solid extract of logwood is used, 15 parts are dissolved in 1,000 parts of water, and 1 part of potassium chromate added.

Runge claimed for this ink the advantage of yielding permanent black writing, and of not acting upon steel pens.

Göpel † considered that *Runge's* formula had too large a proportion of logwood, as shown by the red-brown edges of drops of the ink on white blotting paper, and advocated the following proportions:—Logwood extract 24, potassium chromate 2, and water 1,000 parts.

In the proportion recommended by *Karmarsch* (1 of chromate to 8 of logwood extract), the ink is too grey, pointing to an excess of the chromate.

Although *Runge* had been able to use his ink continuously for two years, it has been found by others that after a time a coagulation due to some unknown cause may occur.

Stein ‡ made numerous experiments to find a remedy for this, and eventually found that the addition of 4 grains of mercuric chloride to a bottle liquefied the coagulated ink and prevented it from becoming thick again.

Viedt,§ however, asserts that *Stein's* remedy is useless, and that a better remedy is the addition of sodium carbonate, as in *Böttger's* writing and copying ink (*infra*). He found that such ink, when kept in a well-closed inkstand, remained fluid for two years, and hence concluded that the best means of preserving the ink was completely to exclude the air.

Böttger's Modification of Runge's Ink.||—Fifteen parts of logwood extract are dissolved in 900 parts of boiling water, and 4 parts of crystalline sodium carbonate dissolved in the clear decanted solution; a solution of 1 part of potassium chromate in 100 parts of water is finally added.

The writer has prepared ink by each of the above methods.

* *Grundriss der Chem.*, 1847, ii., 205; *Dingler's polyt. Journ.*, 1848, cix., 225.
† *Dingler's polyt. Journ.*, 1859, cli., 80.
‡ *Ibid.*, 1850, cxv., 77.
§ *Ibid.*, 1875, ccvii., 76.
|| *Dingler's polyt. Journ.*, 1859, cli., 431; 1869, cxci., 175.

Runge's original formula gives an ink which yields very black characters, but requires the pen to be frequently filled, or the writing appears faint. The ink kept in a test-tube closed with cotton wool was perfectly liquid after three months, though it then yielded writing with a browner tinge.

A simultaneous experiment in which a drop of formalin had been added to the ink gave analogous results.

Ink prepared at the same time by *Böttger's* modification, and kept in a large well-closed flask (containing air), had a slight mould on the surface and gave dirty brown writing. Hence the addition of phenol or other preservative is essential for this ink.

According to *Viedt*, *Plaster's* "*Chrome Ink Powder*" and *Poncelet's* "*Ink without Acid*," are imitations of *Runge's* original chrome ink.

"A blue-black ink," consisting of logwood decoction and chrome alum, gives writing which is too pale and grey.

*Bichromate Logwood Ink.**—One hundred parts of logwood extract are dissolved in 800 parts of lime water, and when solution is complete, 3 parts of phenol and 25 parts of hydrochloric acid are introduced, and the whole left for thirty minutes on the hot-water bath. It is then cooled and filtered, 30 parts of gum arabic and 3 parts of potassium chromate added, and the ink diluted to make 1,800 parts.

This ink is violet-red in colour, and the writing at first appears reddish-brown, but rapidly darkens, and within five minutes has a bluish-black tint. It keeps well and yields very little deposit, but, owing to the amount of free hydrochloric acid present, it has a considerable action upon steel pens. Thus in one of our experiments a pen left in the ink had lost 4·5 per cent. in weight after six weeks, while the ink itself had become semi-solid.

The basic chloride and acetate of chromium are sometimes used, instead of potassium chromate, in chrome inks in order to lessen the tendency to gelatinise.

Dieterich's School Ink.—*Dieterich* † recommends the following as a cheap and effective ink for school purposes:—200 parts of a 20 per cent. solution of logwood extract are diluted with 500 parts of water and heated to 90° C. A solution of 2 parts of potassium bichromate, 50 of chrome alum, and 10 of oxalic acid in 150 parts of water, is then added, drop by drop, and the mixture maintained at 90° C. for thirty minutes, and then diluted to 1,000 parts and mixed with 1 part of phenol. After standing for two or three days it is decanted, and is then ready for use.

* *Ibid.*, 1882, ccxlv., 475. † *Pharm. Manual*, 1897, p. 685.

Walther * gives the following recipes for the preparation of logwood inks, which would belong to Classes 3 and 4 of the German trade classification (p. 118) :—

	Class 3.	Class 4.
Logwood extract,	24	20
Water,	1,000	1,000
Hydrochloric acid (20°-22° Bé.),	15	13
Potassium bichromate,	15	13
Phenol,	3	2·5

The extract is dissolved in 900 litres of hot water and the bicarbonate in 100 litres of hot water and the two solutions mixed and boiled for fifteen minutes, after which the acid and phenol are added, and the ink left for about eight days and then decanted from the deposit.

HÆMATEIN INKS.—Inks prepared with hæmatein in place of logwood extract have more brilliant shades, but are wanting in lustre, and are readily decomposed on heating.

An alkaline hæmatein ink is prepared by mixing 12 parts of hæmatein with 720 parts of water for two hours at about 20° C., and then decanting the liquid, heating it to 30° C., and adding 3 parts of crystalline sodium carbonate. When cold, 0·5 part of potassium chromate in 48 parts of water is gradually added with constant stirring, and lastly 12 parts of gum and 0·5 part of phenol, with sufficient water to make 960 parts of ink in all.

Schmieden's Acid Hæmatein Ink consists of 24 parts of hæmatein dissolved in water (760 parts) at a temperature not exceeding 39° C., then acidified with 80 drops of strong sulphuric acid, mixed with a solution of 4 parts of ferrous sulphate in 48 parts of water, 12 parts of hydrochloric acid, and diluted to 960 parts, a sufficient quantity of gum being subsequently added.

This ink is dark red in colour, and gives dark red writing, which changes to brown and then to black within twelve hours.

For other formulæ of logwood inks see *Copying Inks*, Chap. xii.

USE OF LOGWOOD IN PATENT INKS.—Logwood frequently occurs as an ingredient of patented inks. Thus it is used in *Whitfield's Indelible Safety Ink* (Eng. Pat. No. 7474; 1837), and *Scott* (Eng. Pat. No. 8770; 1840) prepared a similar indelible ink, consisting

* *Chem. Zeit.*, 1921, xvl., 432.

of a logwood iron ink with the addition of gum, indigo, Prussian blue, gas-black, and iron nitrate.

In *J. Reade's* patent (Eng. Pat. No. 11,474; 1846), the precipitate obtained by adding metallic salts (iron, copper, potassium dichromate) to logwood extract is incorporated with a printing ink.

In 1856 (Eng. Pat. 342), *C. and G. Swann* claimed an ink prepared by adding potassium dichromate with a sufficient quantity of potassium bicarbonate, potassium chlorate, mercuric chloride, and ammonia to a decoction of logwood.

Underwood (Eng. Pat. No. 1112; 1857) patented a logwood copying paper (see Chap. xii.), and logwood and hæmatoxylin ink powders were claimed by *Cooley* (Eng. Pat. No. 106; 1867), *Byford* (Eng. Pat. No. 974; 1876), and *Grünwald* (Eng. Pat. No. 963; 1881).

Joly (Eng. Pat. No. 4484; 1875) prepared an ink by the action of tungstic acid upon colouring matters, such as those of logwood, elderberries, etc.

Fonseca and Co. (Eng. Pat. No. 859; 1883) used logwood as an ingredient of an indelible carbon ink; and *Frusher* (Eng. Pat. No. 8241; 1885) patented the manufacture of ink from waste logwood and potassium dichromate from dyeing processes.

Vanadium Inks.

The discovery of the fact that ammonium vanadate forms a black ink with gallotannic acid is attributed to *Berzelius*,* but the writer has been unable to discover any reference to the subject either in the *Jahresberichte* or *Lehrbuch* of *Berzelius*. The statement that this ink is of a very permanent character has been copied from one text-book to another, and is still found in different standard works on chemistry.

In 1889 *Appelbaum* † made a number of experiments with inks thus prepared from gall extracts and solutions of pure gallotannic acid, and found that both the ink itself and the writing faded after the lapse of a few weeks. Hence he doubted whether *Berzelius* had ever made any experiments with the ink.

The writer has repeated the work of *Appelbaum* ‡ and can confirm what he says about gall vanadium inks, though he finds that gallotannin gives an ink of somewhat greater permanence than was found to be the case by *Appelbaum*.

It has been shown by *Mitchell* that ammonium vanadate yields

* *Dingler's polyt. Journ.*, 1835, lvi., 237.

† *Ibid.*, 1889, cclxxi., 423.

‡ *Analyst*, 1903, xxviii., 146.

black ink with substances. Thus gallic acid, logwood extract, hæmatoxylin, and pyrogallol combine with ammonium metavanadate to form black inks, whilst phenol, benzoic acid, saccharin, etc., do not form such compounds.

None of these inks, however, has proved satisfactory in the writer's hands. Although they give black writing at once, the characters gradually turn yellow, even when protected from the light. Hence, apart from the question of expense, ammonium vanadate cannot be regarded as a suitable constituent of writing inks.

It has, however, been claimed as an addition to inks in various patents. Thus *Pinkey* (Eng. Pat. No. 2745, of 1871) prepares an ink from an aniline salt with a salt of vanadium or uranium and an oxidising agent; and a similar patent was taken out by *Grawitz* (Eng. Pat. No. 1620; 1875). The use of vanadium is claimed by *Hickisson* as a constituent of a marking ink (Eng. Pat. No. 5122; 1878), and it is also used by *Just, Weiler* and *Heidepriem* in their patent safety ink (Eng. Pat. 16,757; 1890).

Mitchell (*loc. cit.*) has described certain reactions of vanadium enabling vanadates to be readily distinguished from chromates, which are frequently very similar in colour.

Black Aniline Inks.

The formation of aniline black in a fine state of division within the fibres of the paper was described by *Jacobsen* as an indelible ink for writing or marking, though it has chiefly been used for the latter purpose.

Various brands of nigrosine, which are the sodium salts of the sulphonic acids of anilidophenyl-, anilidodiphenyl-, and dianilidodiphenyl-safranin hydrochloride, are used in the preparation of a black writing ink. They are readily soluble in water, and when dissolved in the proportion of about 1 part in 80 yield a solution which flows readily, dries to a good black, and has no action on metallic pens. The solution keeps well, and the writing resists the action of different chemical reagents, although it can be removed or smudged by water, and lacks the permanence of good iron gall ink.

Coupier and Collins' "Indulin ink," * which was awarded a prize in Paris, was a blue-black ink which, according to *Viedt*, contained nigrosine or similar aniline dye-stuffs.

Solutions of nigrosine were sold under the name of "stylographic

* *Dingler's polyt. Journ.*, 1867, clxxxiii., 78.

ink" when first manufactured in 1867, owing to the readiness with which they flowed from stylographic pens.

Particulars of other aniline inks are given under *Coloured Inks* in Chap. vi.

Inks from Benzene Derivatives.

*Fiechter** has described the preparation of inks from benzene derivatives, such as aniline nitrobenzene, nitrobenzoic acid, and similar compounds, which when heated with sulphuric acid, yield coloured substances soluble in dilute solutions of alkalis or alkali carbonates to form inks.

Aniline sulphate yields a bluish-grey ink, chloronitrobenzene, a red-violet ink, and nitrobenzoic acid, a blue ink. The product obtained from aniline can be used for leather, or for printing ink.

* *Chem. Zeit.*, 1911, xxxv., 115, 1066.

CHAPTER VI.

COLOURED WRITING INKS.

CONTENTS.—Historical—**Coloured aniline inks**—Fugitiveness of aniline inks—Patented coloured inks—Analysis of aniline inks and dyes—Separation—Identification—Tests for coloured inks—Quantitative methods of estimating dye-stuffs.

HISTORICAL.—One of the earliest references to the use of a coloured ink is by *Plutarch*, who mentions a red ink (πυρρον βαμμα) with which certain letters were marked on the doors of the *dikasts* in Athens. Red ink compounded with minium or vermilion seems to have been used for the titles of books among the Romans,* and *Sidonius* (vii. 12) states that rubrica (red ochre) was used for the same purpose. It is interesting to note that our word "rubric," which is applied to the titles of subsections printed in red, thus finds its origin.

A reddish-purple ink was prepared by the Romans from the *Murex*, the mollusc which yielded the famous Tyrian dye. *Montfaucon* was of opinion that this was the source of the ink used by the Byzantine Emperors in their signatures to documents. In fact, the use of any red ink was forbidden to any one excepting those of royal blood.†

If the Emperor was still a minor, his guardians signed for him in green ink, the general use of which was probably also interdicted to some extent. According to *Astle*,‡ ink of this colour was frequently used in Latin manuscripts, though rarely found in charters; but his remarks apply to later ages.

The same authority stated that blue and yellow ink seldom occurred in old manuscripts, and that he knew of no instance of the latter being used later than 1200 A.D.

Gold and silver inks were used by both Greek and Roman Emperors at later periods. They probably consisted of the finely divided metals incorporated with some adhesive medium, such

* Ovid, *Trist.*, I., i., 7.

† *Cod. Justin.*, I. (23).

‡ *Origin of Writing*, 1803, p. 209.

as gum. Metallic writing of this character was sometimes burnished or coated with wax.

Wecker (*De Secretis*, 1582) gives details of the composition of ink of different colours, and refers to gold and silver inks.

In the work of *Canneparius* (1660), to which we have frequently referred, various formulæ for coloured inks appear, such as solution of verdigris in vinegar for green ink, etc.

The use of both indigo and logwood as dye-stuffs was forbidden in England in the reign of Elizabeth, and the Act was not repealed until the reign of Charles II. (*vide supra*). After that both dyes gradually came into use as constituents of writing inks, and are now widely employed in the manufacture of black writing inks.

Inks can be made of any desired tint, for a variety of pigments and dye-stuffs are at the manufacturers' disposal; and the discovery of the coal-tar colours, the main credit for which is due to *Perkin*, has increased their resources almost indefinitely, for they are now able to match any ray of the solar spectrum. Before the time of alizarine and aniline (1858) the maker of coloured inks had recourse to the various vegetable and mineral products which have been used from time immemorial for dyeing fabrics. Thus for red he would employ Brazil wood and cochineal, the latter having a disadvantage in the circumstance that caustic ammonia in considerable quantity is necessary to dissolve it, so that it shall remain in solution and flow freely from the pen. But cochineal or carmine inks were expensive, and they, together with Brazil wood and tin-salt red inks, ceased to be manufactured to any great extent when the more brilliant coal-tar colours became available.

OLDER FORMULÆ FOR COLOURED WRITING INKS.—The following recipes, taken from various sources, are typical of the kind of coloured ink prepared from pigments other than aniline dye-stuffs :—

Red Inks.—(i.) Cochineal, 1 oz.; ammonia, 1 oz.; and water, 1 quart; the infusion was decanted after three days, diluted with water to the required intensity of colour, and a little antiseptic added.

(ii.) Brazil wood (powdered), 1 lb.; acetic acid (5 per cent. strength) 1 gallon, boiled until of sufficient colour, and the extract mixed with 8 ozs. of gum, 8 ozs. of alum, and a little antiseptic.

Green Inks.—(i.) Cream of tartar, 1 part; verdigris, 2 parts, boiled with 8 parts of water.

(ii.) Copper acetate, 1 oz. in 1 pint of water.

(iii.) Potassium chromate, 10 parts; hydrochloric acid, 10 parts; alcohol, 10 parts; water, 30 parts. Neutralised with sodium

carbonate after reduction to the chromic salt, mixed with 10 parts of gum, and decanted (*Winckler*).

(iv.) Indigo ink mixed with a 1·25 per cent. solution of picric acid (*Stein*).

Blue Inks.—(i.) Freshly precipitated Prussian blue ground up with a tenth of its weight of oxalic acid, and water gradually added.

(ii.) Indigo carmine, 10 parts; gum, 5 parts; in 75 parts of water.

Purple Ink.—Infusion of logwood mixed with copper acetate, gum arabic and alum (*Normandy*).

Violet Ink.—Indigo blue ink mixed with cochineal ink.

Yellow Inks.—(i.) A decoction of 25 parts of Persian berries (*Rhamnus amygdalinus*, etc.) in 100 parts of a 3 per cent. solution of alum mixed with 4 parts of gum.

(ii.) A solution of gamboge in alcohol (10 : 10) mixed with 5 parts of gum and diluted to 30 parts with water.

(iii.) A 10 per cent. solution of picric acid containing 2 per cent. of gum.

In a *Report* to the *Science and Art Department* in 1888, *Russell* and *Abney* summarised the results of their experiments on the stability of various water-colour pigments exposed for two years to the action of light and dry air. In each case a wash of 8 tints was applied to paper of the same size and quality, and the slips enclosed in glass cylinders, so arranged that free circulation of air took place while dust was excluded.

In the following list, based on these results, the different pigments are arranged in the order of their instability, and those showing a distinct change in hue or depth of colour are marked with an asterisk :—Carmine,* crimson lake,* purple madder,* scarlet lake,* Naples yellow,* olive green,* indigo,* brown madder,* gamboge,* vandyke brown,* Indian yellow,* cadmium yellow, sepia,* aureolin, rose madder, permanent blue, Antwerp blue, madder lake, vermilion, emerald green, burnt umber, yellow ochre, chrome yellow, raw sienna, Indian red, Venetian red, burnt sienna, chromium oxide, Prussian blue, cobalt, ultramarine ash.

When exposed to the action of moist air very few of the pigments remained unaffected, and none of those of organic origin, and the Prussian and Antwerp blues were completely destroyed.

Experiments were also made in which the washes of pigment were protected from the action of atmospheric oxygen and moisture. The vermilion turned black, but this change was attributed to a physical and not to chemical alteration.

In a later series of experiments, to quote *Abney's* words :—

"We took exactly similar tubes, dried the papers very carefully indeed, dried the tube, inserted the papers, put a Sprengel pump to work, and made a vacuum, and then when the vacuum was very complete, sealed off the top and exposed them." Under these stringent conditions only five colours were acted upon in the very least, and the amount of change was almost imperceptible. The five that were changed were vermilion, raw sienna, Prussian blue, purple madder and sepia.

Coloured Aniline Inks.

ANILINE INKS.—Any conceivable kind of red tint, from magenta to the most brilliant scarlet, can now be obtained from the makers of coal-tar colours. Some of these colours are more fitted for ink manufacture than others, those which are the more readily soluble in water being naturally the best. The red, known as Eosine, which was discovered by Caro in 1874, was early recognised as a valuable material for the purpose, and appears to be more used than any other dye-stuff. In aqueous solution Eosine is subject to the formation of a fungoid growth, so that a small quantity of an antiseptic must be added to the ink to keep it in good condition; otherwise its rich colour is liable to change.

As in the case of red inks, the manufacturer has a number of different tints of blue to choose from in the coal-tar colours. They are most tempting substances to employ, for the suitable ones form a true solution with water, and as a general rule nothing beyond water is required to convert them into serviceable inks. The first aniline colour which was tried for the purpose was Hoffmann's Violet, discovered in 1863, a dye-stuff of such high tinctorial value that an ink composed of 1 part of it in 200 parts of water not only gives a most vivid colour, but will afford by pressure three or four good copies.

FUGITIVENESS OF ANILINE INKS.—Instances of the instability of ink of this character, which was, at one time, largely employed for typewriting, are given in a letter to the *Scientific American* (Ap. 18, 1903). The writer states that typewritten documents, after being stored for six months in a slightly damp place were illegible, with the exception of the gall ink signatures.

In another case a letter-book was wetted with water used to extinguish a fire, and the signatures (in gall ink) were all that remained of 100 pages of correspondence.

It was also shown by *Cross* and *Bevan** that all the aniline colours examined by them when used as dyes on fabrics faded more or less on exposure to sunlight, whilst Eosine and Methylene Blue were especially fugitive.

Of recent years aniline dye-stuffs of a much more permanent nature have been used for writing and printing inks and typewriting inks usually contain fairly stable pigments. The subject is further discussed in Chap. xi.

The following tables give some of the aniline dye-stuffs supplied by the *Badische Company, Ltd.*, for coloured inks.

See also *Aniline Black Inks*, Chap. v. ; *Copying Inks*, Chap. xii. ; and *Ink Powders*, Chap. xvi. *Printing Inks*.

From information kindly given to the writer by *British Dyes, Ltd.*, ink manufacturers can obtain supplies of the following dye-stuffs of English origin :—

Ponceau Scarlet, Cotton Scarlet, Acid Green GG (in place of Diamond Green G), Malachite Green Crystals Y (in place of Diamond Green B), Indigo Carmine, Soluble Blue, Acid Violet, Fast Yellow and Tartrazine.

The usual proportions that we have found to yield suitable solutions for writing inks are about 1 gramme in 50 to 80 c.c. of water, according to the tinctorial power of the particular dye-stuff. The inks thus made are very fluid, and in this respect particularly suitable for stylographic and other descriptions of fountain pens. If a suitable dye-stuff is used there will be no precipitation, and therefore no suspension of particles in the liquid. There is, therefore, no need to add gum to inks of this description ; indeed, such an addition would tend to counteract one of their most valuable properities—their fluidity. It is necessary to mention this point, because we have found many published formulæ for aniline inks in which sugar or gum is erroneously included as a necessary constituent.

PATENT COLOURED INKS.—*Reade*, in his patent (No. 11,474 ; 1846), claimed the use of inks containing "soluble Prussian blue," prepared in a specified manner, and of a red ink prepared from cochineal. A lake of cochineal extract and alum dissolved in ammonia solution was also claimed by *Wood* in 1885 (Eng. Pat. No. 1676).

The use of aniline dyes was first claimed in this country by *Croc* in 1861 (Eng. Pat., No. 2972), and in the following year by *Annaud* (Eng. Pat., No. 675 ; 1862). Pigments from aniline waste were proposed as the source of writing inks by *de la Rue* (Eng. Pat., No. 2235 ; 1862), whilst aniline dye-stuffs were again patented by

* *Journ. Soc. Arts*, 1891, xxxix., 152.

Aniline Dye-stuffs suitable for Writing Inks

Colour.	Trade name.	Scientific.
Red.	Eosine, Erythrosine and Phloxine.	Alkali salts of bromine and iodine compounds of fluorescëin and of dichlorfluorescëin.
	Ponceau Scarlet.	Alkali salts of xylidin-azo- and cumidin - azo - naphtholdisulphonic acids.
	Cotton Scarlet.	Sodium salt of amido-azo-benzol-azo-naphtholdisulphonic acid.
Green.	Neptune Green S.G.	A triphenylmethane dye-stuff.
	Light Green S.F. (yellowish).	Sodium salt of diethyl-dibenzyl-diamidotriphenyl carbinol trisulphonic acid.
	Light Green S.F. (blueish).	Sodium salt of the dimethyl compound.
	Diamond Green G. & B.	Salts of tetra-ethyl- and tetra-methyl-di - para - amido - triphenyl carbidrides.
Blue.	Indigo Carmine.	Indigotin sodium disulphonate.
	Soluble Blue T.	Salts of triphenylrosanilin and triphenylpararosaniline-trisulphonic acids.
Violet.	Acid Violet 4 B.L.	Sodium salt of tetraethyldibenzyl-pararosaniline-disulphonic acid.
Yellow.	Fast Yellow.	Mixtures of the sodium salts of amidoazobenzoldisulphonic, monosulphonic, and amido-azotoluoldisulphonic acids.
	Tartrazine.	Sodium salt of diphenyl-parasulphonic acid or of azo-dioxytartaric acid.

Jefferies in 1879 (Eng. Pat., No. 3391). For other patents in which coloured pigments are claimed see *Copying Inks*, *Sympathetic Inks*, *Printing Inks*, and *Ink Powders*.

ANALYSIS OF ANILINE INKS AND DYES.—Several schemes for the identification of dye-stuffs have been published. Among those most frequently employed are the methods of *Rota*,* of *Weingartner*, and of *Green*, in which the dyes are separated into well-defined groups in accordance with their constitution, and then subdivided by their behaviour with separate reagents.

ROTA'S METHOD.—The aqueous solution (*e.g.*, the ink) or an alcoholic solution of the dye is diluted to about 1 : 10,000, and 5 c.c. shaken with 4 to 5 drops of strong hydrochloric acid and 4 to 5 drops of 10 per cent. stannous chloride solution. If necessary, the liquid is heated to boiling-point, and the test repeated after further dilution of the dye-stuff solution.

Classification of Organic Colouring Matters.

A portion of the dilute aqueous or alcoholic solution is treated with HCl and $SnCl_2$.

<table>
<tr><td colspan="2">Complete decolorisation. Reducible colouring matters.
The colourless solution is treated with ferric chloride or shaken in contact with air.</td><td colspan="2">No change further than with HCl alone. Non-reducible colouring matters.
Part of the original solution is warmed with 20 per cent. KOH.</td></tr>
<tr><td>The liquid remains unchanged.
Colouring matters not re-oxidisable.</td><td>The original colour restored.
Re-oxidisable colouring matters.</td><td>Decolorisation or a precipitate.
Imido-carbo-quinone colouring matters.</td><td>No precipitation. Colour increased.
Oxy-carbo-quinone colouring matters.</td></tr>
<tr><td>Class I</td><td>Class II</td><td>Class III</td><td>Class IV</td></tr>
<tr><td>Nitro-, nitroso-, and azo-dyes, including azoxy- and hydrazo-dyes.</td><td>Indogenide- and imido-quinone dye-stuffs.</td><td>Amino derivatives of di- and tri-phenyl-methane, auramines, acridines, and quinolines.</td><td>Non-amide di-phenyl-methane dye-stuffs, oxy-ketone, colouring matters (most of the natural colouring matters).</td></tr>
</table>

* *Chem. Zeit.*, 1898, xxii., 437.

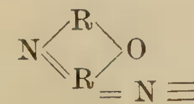
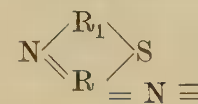
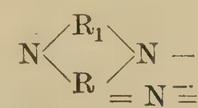
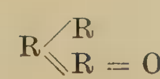
Class I. Reduced by HCl + $SnCl_2$ and not Re-oxidisable

NITRO-COLOURING MATTERS: $R - NO_2$. Yellow or orange. Soluble in water. Wool and silk dyed directly, but not cotton. The aqueous solution shows tendency to decolorisation with HCl. With HCl + $SnCl_2$ partially reduced, giving red nitro-amido derivatives (nitramines) or nitro-phenols turning red in KOH.	NITRAMINES. Soluble in ether in presence of KOH.			$-N = R = N \langle {}^{O}_{OH}$	*e.g.* Aurantia.
	NITRO-PHENOLS. Insoluble in ether in presence of KOH.	*Non-sulphonated.* Soluble in ether in presence of acetic acid.		$O = R = N \langle {}^{O}_{H}$	Victoria yellow.
		Sulphonated. Insoluble in ether.			Naphthol yellow.
NITRO-COLOURING MATTERS: $O = R = N - OH$. Brown or green, usually insoluble in water. Indirect for fibres. With H_2SO_4 + C HOH give blue colour (Liebermann's reaction).	*Non-sulphonated.* Insoluble in water. Soluble in alcohol. Soluble in ether in presence of acetic acid.				Dioxime (L.)
	Sulphonated. Soluble in water. Insoluble in ether.				Naphthol green.
AZO-COLOURING MATTERS: $R - N = N - R$. Their aqueous solution decomposed with KOH and extracted with ether, gives an ethereal extract with the annexed characteristics.	Coloured; shaken with dilute acetic acid yields to it the original colour. BASIC COLOURING MATTERS.	NON-SULPHONATED. AMIDO-AZO COLOURING MATTERS.		$-N = R = N - NHR_1$	Bismarck brown.
	Coloured solution; not yielding its colour to dilute acetic acid. NEUTRAL COLOURING MATTERS.	OXYAZO-COLOURING MATTERS, WITHOUT CARBOXYL.		$O = R = N - HR_1$	Sudan I. (A).
	Colourless solution. Yields nothing to acetic acid. ACID COLOURING MATTERS.	*Non-sulphonated.* Extracted by ether from dilute solution in acetic acid.	OXYAZO-COLOURING MATTERS WITH CARBOXYL GROUP	Indirect for cotton wool.	Diamond yellow (By).
				Direct for cotton wool.	Chrysamine.

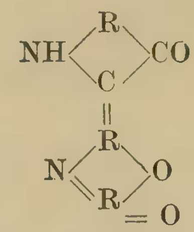
Class I. Reduced by HCl + $SnCl_2$ and not Re-oxidisable—(continued).

AZO-COLOURING MATTERS: $R - N = N - R$ Their aqueous solution decomposed with KOH and extracted with ether, gives an ethereal extract with the annexed characteristics.	Colourless solution. Yields nothing to acetic acid. ACID COLOURING MATTERS.	*Sulphonated.* Not extracted by ether from solution in dilute acetic acid.	NON-AMIDO COMPOUNDS. Unaltered by HNO_2.	Indirect for cotton wool.	Bordeaux B (A).
				Direct for cotton wool.	Azo-blue (A).
			AMIDO COMPOUNDS. Changed by HNO_2.	Indirect for cotton wool.	Solid yellow N (P).
				Direct for cotton wool.	Congo red (A).

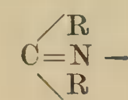
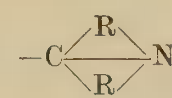
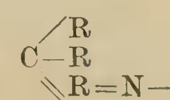
Class II. Reduced by HCl + $SnCl_2$ and Re-oxidisable

The aqueous or alcoholic solution is treated with KOH and extracted with ether. The ethereal solution washed with water has the annexed characteristics.	The ethereal solution is coloured or colourless, and yields the original colour to 5 per cent. acetic acid. BASIC COLOURING MATTERS. Fixed on wool in alkaline bath.	The solution is readily reduced by HCl + $SnCl_2$ in the cold.	OXYAZINES (no sulphur).		Nile blue A (B).
			THIAZINES (sulphur).		Methylene blue.
		The coloured solution is reduced but slowly and incompletely, even on warming, and with the addition of much $SnCl_2$ + HCl.	INDULINES. Blue colour with conc. H_2SO_4. Blue on dilution.		Induline. Soluble in alcohol.
			SAFRANINES. Green colour with H_2SO_4. On dilution blue, then violet.		Safranine T. Extra (A).
	Coloured. Does not yield the colour to acetic acid.	Blue colouring matters changed by HCl on warming.	INDOPHENOLS.		Indophenol.

Class II. Reduced by HCl + $SnCl_2$ and Re-oxidisable—(continued)

The aqueous or alcoholic solution treated with KOH and extracted with ether. The ethereal solution washed with water has the annexed characteristics.	NEUTRAL COLOURING MATTERS. Insoluble in water. Soluble in alcohol. Fixed on fibres in bath.	Red or blue colouring matters. Unaltered by HCl. With HNO_3 yield isatin.		INDOGENIDES.		Indigotin.
	Uncoloured. Yield nothing to acetic acid.	*Non-sulphonated.* Soluble in ether in presence of acetic acid.		OXAZONES.		Fluorescent blue, Orceïn.
	ACID COLOURING MATTERS. Soluble in water. Fixed on wool in acid bath.	*Sulphonated.* Insoluble in ether under all circumstances.	Reduced by $SnCl_2$ + HCl.	SULPHONATED INDOGENIDES.		Indigo carmine.
				SULPHONATED THIAZINES.		Thiocarmine R (C).
			Not reduced by $SnCl_2$ + HCl.	SULPHONATED INDULINES.		Soluble nigrosin.

Class III. Colouring Matters not Reduced by $SnCl_2$ + HCl. Containing the Imido quinone Carbon Chromophore $- N = R = C =$

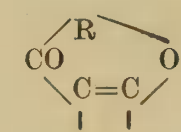
The aqueous or alcoholic solution treated with KOH and extracted with ether.	The ethereal solution is colourless or coloured. The colour is yielded to 5 per cent. acetic acid.	Colourless, non-fluorescent, ethereal solution. Yellow colour yielded to acetic acid non-fluorescent. The aqueous solution is decolorised by KOH and decomposed by HCl.	AURAMINES.		*e.g.* Auramine O (B).
		Colourless, ethereal solution. Green fluorescence. Aqueous solution precipitated by KOH, hardly altered by HCl. Turns red with HNO_3.	ACRIDINES.		Phosphine.
	BASIC COLOURING MATTERS. Fixed on wool in alkaline bath (NH_3).	Colourless, or coloured ethereal solution. Non-fluorescent. Colour yielded to acetic acid—reddish-violet, blue, and green without fluorescence. Aqueous solution usually decolorised on warming with KOH, and coloured yellow by HCl (excepting fuchsine).	FUCHSINES (non-sulphonated).		Fuchsine.

Class III. Colouring Matters not Reduced by $SnCl_2 + HCl$. Containing the Imido quinone Carbon Chromophore $-N=R=C=$—(continued)

The aqueous or alcoholic solution treated with KOH and extracted with ether.

Basic Colouring Matters—*continued*		Ethereal solution colourless and non-fluorescent. Acetic acid coloured rose and fluoresces. Aqueous solution decolorised with KOH.	Pyronines (coloured yellow by HCl. Direct for cotton wool).	$-C\langle^{R}_{R}\rangle O$, $=N-$	Pyronine (G).
			Rhodamines (non-sulphonated). Unaltered by HCl.		Rhodamine S (By).
The coloured ethereal solution does not yield its colour to acetic acid. Neutral Colouring Matters. Insoluble in water. Soluble in alcohol.		The ethereal solution is yellow, and non-fluorescent. Alcoholic solution yellow, non-fluorescent, and unaltered by aqueous acids and alkalies.	Quinone-phthalones.	$-C\langle^{R}_{R=N\equiv}$	Quinoline yellow A (soluble in alcohol).
Ethereal solution colourless. Yields nothing to acetic acid. Acid Colouring Matters. Soluble in water. Fixed on wool in acid bath (HCl).	The aqueous solution heated with fat-free wool to boiling. Does not dye the wool.	Yellow colouring matters. No fluorescence in water. Unaltered by aqueous acids and alkalies.	Sulphonated Quinone-phthalones.		Quinoline yellow A (soluble in water).
		Reddish-violet, blue, or green colouring matters. Usually decolorised by KOH, little changed by HCl.	Sulphonated Fuchsines.		Fuchsine S (B).
		Red or violet colouring matters. Soluble in water with fluorescence. Precipitated by HCl. Changed but little, or not at all, by KOH.	Sulphonated Rhodamines.		Violamine R (M).
	Dyes the wool.	Brownish-yellow or orange colouring matters. Aqueous solution $\pm$ fluorescent. Fixed directly on silk, wool, and cotton.	Thiazoles.	$-C=N$, $S-R$ (C–S and N–R bonded)	Primulin (B).

Class IV. Colouring Matters not Reduced by $SnCl_2 + HCl$. Containing the Oxy-quinone Carbon Chromophore $- O = R = C =$

The alcoholic solution of the colouring matter, treated with a few drops of a dilute solution of Fe_2Cl_6 (1 : 1000).						
Remains unaltered. NON-AMIDO TRIPHENYL-METHANE COLOURING MATTERS usually soluble in water and direct for wool.	The colouring matter is dissolved or suspended in boiling water.	Not directly fixed on wool. Most of them insoluble in water. Soluble in alcohol without fluorescence.	AURINS.	$C\begin{cases}/R^1\\ -R^1\\ \backslash\backslash R = O\end{cases}$	Aurin.
		Fixed directly on wool. Most of them soluble in water and alcohol. Fluorescence.	PHTHALEINS.	$C\begin{cases}/R^1\diagdown\\ -R^1/O\\ \backslash\backslash R = O\end{cases}$	Eosin.
Changes to green or olive-green. OXY-KETONE COLOURING MATTERS. Most of them insoluble in water, and indirect for fibres.	The original colouring matter is treated with faintly alkaline water (KOH, 1 per cent.). Dissolves with yellow or reddish-yellow colour. MONO-KETONES.	The alkaline solution treated with excess of HCl. Inclined to decolorisation, especially on warming (with decomposition).	BENZOPHENONES.	$CO\begin{cases}/R\\ \backslash R\end{cases}$	Alizarin yellow A (B).
		Coloured intense yellow without decomposition.	FLAVONES.		Quercetin.
	Dissolves with red, reddish-violet, violet, green, or blue colour. DIKETONES (quinones).	The alkaline solution acidified with acetic acid. The free colouring matter precipitated. Usually soluble in ether, and indirect for fibres.	NON-SULPHONATED ANTHRAQUINONES.	$CO\langle{}^{R}_{R_1}\rangle CO$	Alizarin.
		Colouring matter remains in solution. Insoluble in ether, fixed directly on wool.	SULPHONATED ANTHRAQUINONES.		Sulphonated alizarin (alizarin-red).

METHODS OF WEINGARTNER AND GREEN.—Molinari * gives the following outline embodying the methods of *Weingartner and Green.*

I. *Dye-stuffs Soluble in Water.*—Add to aqueous solution 10 per cent. solution of tannin and 10 per cent. solution of sodium acetate.

A. *Precipitate indicates Basic Colouring Matters.*

(*a*) Treat solution with Zn and HCl; put a few drops of decolorised liquid on filter paper, and wave the paper in the air.

(i.) Re-appearance of original colour indicates: Azines, Oxazines, Thiazines, and Acridines (*e.g.*, Pyronine, Safranine, Rosinduline, Benzoflavin, Indulin, etc.).

(ii.) Re-appearance of original colour after moistening with one drop of 1 per cent. chromic acid solution indicates: Rhodamines, or dyes containing a triphenylmethane group.

(iii.) Non-appearance of original colour indicates: Auramine, Thioflavin, Chrysoidin, Janos Colours, Bismarck Brown.

B. *No Precipitate with Tannin. Acid Dye-stuffs.*

(*b*) Reduce the solutions as in (*a*) or with Zn and NH_3, and place drop on paper and wave in air.

(i.) Re-appearance of original colour indicates: Sulphonic or Mordant dyes belonging to Azines, Oxazines, Thiazines, soluble Indulin, Nigrosines or Azocarmine, Thiocarmine, Indigocarmine, Gallocyanine, Mikado Orange.

(ii). Re-appearance after treatment with chromic acid or gaseous ammonia. Acidify original solution with H_2SO_4, and shake with ether. Ether extracts: Phthaleins, Auramines. Non-coloration of ether; Triphenylmethane dyes.

(iii.) Non-coloration on heating the paper or treatment with ammonia vapour, indicates azo-, nitro-, nitroso-, or hydrazine colours, which, when burnt in powder, give coloured vapours (*e.g.*, Naphthol Yellow S., Picric Acid, Victoria Yellow).

(iv.) Red-brown colour on reducing the solution, changing to original colour in the air indicates Alizarine S., Alizarine Blue S and the like.

(v.) No decolorisation (or practically none) with zinc and ammonia or zinc and HCl indicates Thiazole Yellow, Mimosa, Quinoline Yellow S., Primuline, Thioflavin S., Chloramine Yellow, etc.

II. *Sulphur Dye-stuffs.*—These are precipitated when treated with water and dilute HCl, and emit hydrogen sulphide (detected by lead acetate paper). They are redissolved by 10 per cent. sodium sulphide solution.

* *Organic Chemistry*, 1913, p. 671.

III. *Dye-stuffs insoluble in Water.*—Moisten and treat with two drops of 5 per cent. sodium hydroxide solution.

(*a*) If it dissolves, it should be reduced with zinc dust and ammonia, and filter paper dipped in the liquid and exposed to the air.

(i.) Rapid re-appearance of the colour indicates: Cœrulein, Gallo-cyanine, Gallein, Galloflavin, Alizarine Blue, Black, or Green.

(ii) Non-appearance of the colour indicates alizarine derivatives, Alizarine, Nitrosonaphthol, Nitrosoresorcinol, Soudan Brown, etc.

(*b*) Insoluble in NaOH but soluble in 70 per cent. alcohol.

(i.) Fluorescent solution which on treatment with 33 per cent. NaOH either disappears (Magdala Red) or does not disappear (alcohol-soluble Eosine, Cyanosine).

(ii.) Solution not fluorescent, but coloured red-brown by 33 per cent. NaOH: Alcohol-soluble Induline, Alcohol-soluble Nigrosine, Alcohol-soluble Aniline Blue.

(iii.) The solution remains fluorescent: Indophenol.

(*c*) Colouring matters insoluble in NaOH and 70 per cent. alcohol, Indigo, Alizarine Black, Sulphur Colours (soluble in sodium sulphide).

SEPARATION OF COLOURING MATTERS IN A MIXTURE.*—Free dye-stuffs, but not their salts, can frequently be extracted with ether or fixed upon wool. It is also possible in certain cases to effect a separation by treating the mixture with cold or hot alcohol or water.

Extraction with Ether.—By adding potassium hydroxide to a dilute aqueous solution of the mixture and shaking the liquid with ether, basic dye-stuffs are extracted, whilst acid dye-stuffs remain in the aqueous layer. The ethereal extract is washed with faintly alkaline water, and then shaken with a third of its volume of 5 per cent. acetic acid, which will extract the dye-stuff and, when evaporated on the water-bath, will leave it as a residue.

A few acid or neutral dye-stuffs may also be extracted by alkaline ether, as for example, Quinoline Yellow, Indophenol Blue (soluble in alcohol), the various Soudans, etc.

Different alkalis have different liberating capacities for basic dye-stuffs. Safranine requires potassium hydroxide, whilst for Magenta, ammonia is sufficient. Others, again (Indulines, Oxyazines and Acridines), are liberated by very dilute ammonia; and others (*e.g.*, Chrysoidine, Bismarck Brown, Rhodamine S (By), Victoria Blue, etc.) are dissociated in aqueous solution.

Hence a separation may often be effected by successively shaking

* Rota, *loc. cit.*

the aqueous solution with ether, first alone, then in presence of 1 per cent. of ammonia, then with concentrated ammonia, and finally with 20 per cent. potassium hydroxide.

Sometimes a further separation may be effected by shaking the ethereal solution with water. In this way Acridine Yellow may be separated from the very similar Phosphine.

The acid dye-stuffs not extracted from an alkaline solution by ether may be separated by similar methods of successive extraction into three groups :—(1) Those extracted by ether in the presence of hydrochloric or sulphuric acid. (2) Those soluble in ether in the presence of those acids. (3) Those insoluble in ether.

In this way Erythrosine may be separated from Roccellin, and from Bordeaux B ; and Direct Yellow (A) from Congo Brown R (A) and from Congo Red (A).

By treating the ethereal solutions with water and dilute ammonia, further separations may be effected, as for example, Picric Acid from Martius' Yellow.

Separation by means of Wool.—When a separation cannot be effected by means of ether, fixation upon wool is often possible. An aqueous solution of the colouring matter (1 : 1,000) is treated with 4 or 5 drops of ammonia solution per 100 c.c., some wool added, and the liquid boiled, with constant stirring. This treatment is repeated with fresh quantities of wool, so long as the fibres are dyed. The wool is washed with boiling ammoniacal water and then with hot water, and extracted with hot 5 per cent. acetic acid. On evaporating the acid extract on the water-bath, the basic dye-stuffs are left.

Wool is more effective for the separation of acid colouring matters, some of which are fixed directly upon it. The solution (0·1 per cent.) of the colour is acidified with hydrochloric acid (3 to 4 drops per 100 c.c.) heated to boiling-point and the wool immersed in it for 3 to 5 minutes, with continual stirring. This treatment is repeated so long as colour is fixed upon the wool. The dyed wool is then washed with acidified water and with pure water, and the colour extracted with 5 per cent. ammonia solution. By boiling the liquid until ammonia is expelled, the dye-stuff is left in neutral solution.

Since some of the indirect dye-stuffs are also taken up to a slight extent by the wool fibre, this solution should also be treated with wool to effect a complete separation. In this way it is possible to separate the following dye-stuffs and colouring matters :—

Direct :	Bordeaux B (A)	Biebrich scarlet	Acid yellow (A)
Indirect :	Œnocyanin	Cochineal	Saffron

The direct dyes vary in their affinity for wool. With some (*e.g.*, those containing oxysulpho groups) the wool is readily dyed in strongly acid solution, whilst with others (both acid and basic) it is dyed in a neutral solution.

The following colouring matters may thus be separated :—

Fixed in neutral bath :	Alkali violet (B)	Acid violet 4 BN	Archil
Fixed in acid bath :	Ponceau 6 RB (A)	New coccine (A)	Bordeaux B (M)

By using a strong hydrochloric acid solution (1 : 200) the following separations may be made :—

Fixed in strong acid bath :	Bordeaux S (A)	Bordeaux B (A)
Fixed in weak acid bath :	Orange G (A)	Methyl orange

When wool fails to effect the separation of a mixture cotton wool is sometimes effective in fixing certain dyes. For example :—

Direct for cotton :	Carbazol B	Cotton yellow
Indirect for cotton :	Diamond yellow R (By)	Phloxine B (B)

Here, too, the acidity and concentration of the bath have an influence on the fixation. For example, in a weak (HCl) acid bath Brilliant Congo (A) is readily fixed, whereas Brilliant Yellow (A) is only fixed upon the cotton with difficulty.

If none of these methods has effected a separation, other solvents, such as petroleum spirit, amyl alcohol, chloroform, etc., may be tried. With petroleum spirit, for example, Eosine may be separated from Martius' Yellow.

For the identification of the separated dyes recourse may be had to the tables given above, and to tabulated properties of individual dye-stuffs given in various text-books.*

SCHLUTTIG'S TESTS FOR COLOURED INKS.†—The following tables show the reactions given by different groups of typical coloured inks, and by iron-gall inks containing dye-stuffs to give the respective provisional colours. In each case the inks are diluted with an equal volume of water, and a series of stripes prepared by the "stripe method." These are allowed to dry for at least a day, exposed to pure air, and then tested with a drop of the respective reagents, the alterations in colour being recorded immediately, and also after the lapse of twenty-four hours.

* *E.g.*, Molinari's *Organic Chemistry*.

† These tables from *Lunge's Technical Analysis*, are given here by the kind permission of Dr. C. A. Keane, the editor of the English edition.

I. Blue and Blue-Black Inks.

1. Soluble Prussian blue from 0·3 per cent.
2. Sodium indigo-sulphonate, 0·1 per cent.
3. Bavarian blue, DSF, 1·2 per cent.
4. Methylene blue, 0·5 per cent.
5. Blue-black ink.

	Sodium hydroxide, 2.5 per cent.	Sulphuric acid, 5 per cent.	Oxalic acid, 1.5 per cent.	Sodium carbonate, 5 per cent.
1. Immediately	White	Unchanged	Unchanged	White
After 24 hours	White, with yellow edge	Darker blue	Darker blue	,,
2. Immediately	Yellow	Unchanged	Unchanged	Lighter blue
After 24 hours	White, with yellow edge	White	White	Light grey-blue
3. Immediately	Brown	Darker blue	Darker blue	Black-blue
After 24 hours	White, with yellow edge	,,	,,	Light yellow, with green edge
4. Immediately	Violet	Lighter blue	Lighter blue	Light blue
After 24 hours	Green-blue, with green edge	White, with green edge	,,	Green-blue
5. Immediately	Brown	Lighter blue	Lighter blue	Brown-blue
After 24 hours	,,	Grey-blue	,,	Brown

	Sodium bisulphate, 5 per cent.	Sodium sulphite, 5 per cent.	Potassium oxalate 5 per cent.	Stannous chloride, 5 per cent. + Hydrochloric acid, 5 per cent.
1. Immediately	Unchanged	Violet blue	Light grey	Unchanged
After 24 hours	Darker blue	White to light grey	White	,,
2. Immediately	Unchanged	Lighter blue	Unchanged	White
After 24 hours	White	White	Light blue-grey	,,
3. Immediately	Darker blue	,,	Unchanged	Unchanged
After 24 hours	,,	,,	Light blue-green	Darker blue
4. Immediately	Lighter blue	Lighter blue	Lighter blue	White
After 24 hours	,,	Light blue	Light blue	,,
5. Immediately	Light blue	Red-grey	Unchanged	Light blue
After 24 hours	,,	Brown	Brown	Grey-blue with green edge

II. Green and Green-Black Inks

	Ammonia solution, 5 per cent.	Sodium hydroxide, 2.5 per cent.	Sodium carbonate, 5 per cent.	Sodium sulphite, 5 per cent.
6. Immediately	White	White	Lighter green	White
After 24 hours	Light green	White, with yellow edge	White	,,
7. Immediately	Light green	Light green	Lighter green	Light green
After 24 hours	,,	White, with yellow edge	Light green	Pale green
8. Immediately	Green-brown	Brown	Brown-green	Grey-green
After 24 hours	,,	,,	Brown	Brown

	Borax, 5 per cent.	Nitric acid, 5 per cent.	Sulphuric acid, 5 per cent.
6. Immediately	Light green	Light green	Light green
After 24 hours	White	White, with grey edge	White
7. Immediately	Unchanged	Light yellow-green	Light yellow-green
After 24 hours	Lighter green	White, with grey-green edge	White, with yellow edge
8. Immediately	Grey-brown	Light blue-green	Light blue-green
After 24 hours	Brown	Grey-blue	Green-blue

6. Acid green, 1·2 per cent.
7. Malachite green, 0·2 per cent.
8. Typical green-black ink.

III. Red and Red-Black Inks.

9. Nacarate S, 0·5 per cent.
10. Fuchsine F, 0·2 per cent.
11. Eosine A, 1·5 per cent.
12. Carmine, 1·65 per cent. + ammonia, 0·7 per cent.
13. Typical red-black ink.

	Sodium hydroxide, 2.5 per cent.	Sulphuric acid, 1.5 per cent.	Oxalic acid solution 1.5 per cent.
9. Immediately	Yellow-grey	Unchanged	Unchanged
After 24 hours	White, with grey-red edge	Grey-red	Light grey-red
10. Immediately	Light red	Light grey	Unchanged
After 24 hours	Pale red	White	Light blue-grey
11. Immediately	Yellow red	Light yellow	Yellow
After 24 hours	White, with orange-red	,,	,,
12. Immediately	Red-grey	Unchanged	Unchanged
After 24 hours	White, with dark red edge	Brown-red	,,
13. Immediately	Grey-red	Light red	Light red
After 24 hours	Brown	,,	,,

	Sodium carbonate solution, 5 per cent.	Sodium bisulphate 5 per cent.	Stannous chloride and hydrochloric acid.
9. Immediately	Red-grey	Unchanged	Unchanged
After 24 hours	,,	Light red	Bright grey, with violet edge
10. Immediately	Unchanged	Red-grey	White
After 24 hours	,,	Light blue-grey	White, with dark green edge
11. Immediately	Yellow-red	Yellow	Light yellow
After 24 hours	,,	,,	,,
12. Immediately	Red-grey	Unchanged	Unchanged
After 24 hours	,,	,,	,,
13. Immediately	Brown	Light red	Light red
After 24 hours	,,	,,	White, with red edge

IV. Violet and Brown Inks.

14. Methyl violet, 0·3 per cent.

15. Chrome logwood ink, containing 2 per cent. logwood extract, 0·3 per cent. of potassium chromate, and 2 per cent. of sodium carbonate.

16. Tungsten ink, containing 4·5 per cent. of logwood extract, 1·56 per cent. of sodium tungstate, 0·4 per cent. of tartaric acid, and 0·03 per cent. of salicylic acid.

17. Logwood copying ink, containing 8 per cent. of logwood extract, 2 per cent. of aluminium sulphate, 0·5 per cent. of oxalic acid, 4 per cent. of ammonium oxalate, 1 per cent. of glucose, 0·5 per cent. of potassium dichromate, and 0·15 per cent. of salicylic acid. Dries violet-black.

18. Alizarine, 2·5 per cent., and ammonia solution, 1·0 per cent. Dries brown.

	Ammonia solution, 5 per cent.	Sodium hydroxide, 2.5 per cent.	Sulphuric acid, 5 per cent.	Sodium sulphite, 5 per cent.
14. Immediately	Unchanged	Violet	Light green	Light violet
After 24 hours	Light violet	Light grey	Yellow-grey	,,
15. Immediately	Unchanged	Light yellow	Grey-red	Unchanged
After 24 hours	,,	Grey-yellow	Grey-red, with dark red edge	Light grey
16. Immediately	Red-blue	Grey-violet	Red-violet	Light yellow
After 24 hours	Violet-black	Grey-yellow, with brown edge	Dark red	,,
17. Immediately	Blue	Brown, with blue edge	Yellow-red	Grey-violet
After 24 hours	Violet-black	Grey-yellow, with brown edge	,,	Light grey
18. Immediately	Dark red	Blue, with red edge	Light yellow	Violet
After 24 hours	,,	Light brown, with dark edge	,,	Dark red

	Borax, 5 per cent.	Copper sulphate, 5 per cent.	Stannous chloride and hydrochloric acid.
14. Immediately	Unchanged	Unchanged	Light grey-blue
After 24 hours	Lighter violet	Violet	White, with green edge
15. Immediately	Unchanged	Unchanged	Grey-violet
After 24 hours	Light grey	,,	Light grey-red, with dark red edge
16. Immediately	,,	,,	Red-violet
After 24 hours	,,	Blue-black	Dark red
17. Immediately	Blue	Dark grey-blue	Red-violet
After 24 hours	Light violet	Blue-black	Dark red
18. Immediately	Red-brown	Brown	Yellow
After 24 hours	Dark red	,,	,,

V. Black Inks.

	Sodium hydroxide, 2.5 per cent.	Sodium carbonate, 25 per cent.	Sulphuric acid, 5 per cent.	Sodium sulphite, 5 per cent.	Stannous chloride.
19. Immediately	Brown-red	Grey-violet	Dark blue	Yellowish red	Dark blue
After 24 hours	Red-grey, with dark red edge	Grey-red	Dark blue, with violet edge	Light brown	,,
20. Immediately	Light grey	Violet-grey	Grey	Violet-grey	Blue-grey
After 24 hours	,,	,,	Grey-blue	,,	,,
21. Immediately	Brown	Brown	,,	Brown-violet	,,
After 24 hours	,,	,,	,,	Brown	Grey-blue
22. Immediately	Green-blue	Bluish-green	Light grey	Unchanged	Grey-yellow
After 24 hours	Yellow-grey	,,	Light yellow-grey	Brown	,,
23. Immediately	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged
After 24 hours	,,	,,	,,	,,	,,

19. Black ink containing 1·2 per cent. of Bavarian blue, 0·3 per cent. of acid green, 1·5 per cent. of chestnut brown. Flows blue-black and dries grey-black.

20. Nigrosine ink, containing 1·25 per cent. of nigrosine.

21. Typical iron-gall ink.

22. Vanadium ink containing 10 per cent. of tannin and 0·4 per cent. of ammonium vanadate. Dries grey-green.

23. Carbon ink containing 10 per cent. of lampblack, 6·5 per cent. of shellac, and 6·5 per cent. of borax.

None of the foregoing inks resisted the action of sodium hypochlorite, with the exception of No. 23, the pigment of which consisted of lampblack. All the others were immediately bleached.

The reagents mentioned in the preceding tables have only been selected as illustrative examples. Obviously many others might be used, and in special cases prove more characteristic.

Quantitative Estimation of Dye-stuffs.

Estimation of Nitro-Compounds.—Knecht * based a method of estimation on the reduction of nitro compounds to amido compounds by means of titanous chloride :—

$$\begin{aligned} -NO_2 + 3H_2 &= -NH_2 + 2H_2O \\ TiCl_3 + HCl &= TiCl_4 + H \end{aligned}$$

The solution of the soluble dye is titrated directly, the change in colour indicating the end of the reaction.

* *J. Soc. Dyers and Col.*, 1903, vi., 19; vii., 19; 1905, iii., 292.

For example, a solution of Crystal Scarlet 6R($C_{20}H_{12}N_2S_2O_2Na_2 + 7H_2O$) containing 0·1 grm. was boiled for a minute with 10 c.c. of hydrochloric acid, and titrated with standard titanous chloride solution, of which 22·6 c.c. were required for decolorisation—

1 c.c. $TiCl_3$ = 0·0015799 grm. of Fe.
502 grms. of dye = 224 grms. Fe (by theory).

Therefore

$$\frac{0 \cdot 0015799 \times 22 \cdot 6 \times 502}{224} = 0 \cdot 08001 \text{ grm. of dye.}$$

Colorimetric comparison will also be found useful for approximate results. A weighed quantity of the dye is dissolved and the solution matched in colour with the dye in question.

Methods of estimating indigo have been devised by *Rawson* * and by *Bloxam*.†

In *Pelet's* method of estimation a basic dye is precipitated by means of a standard solution of an acid dye, and the end point is found by the disappearance of one or both of the coloured rings formed by spotting on paper. This method has been shown by *Salvaterra* ‡ to give results as good as those by *Knecht's* method, which involves titration in an atmosphere of carbon dioxide.

Titration methods of this kind have been studied by *Brown* and *Jordan*,§ who have found that the following rules must be followed:—(1) The dyestuff to be estimated and the volumetric solution used must be of a different colour in solution—*e.g.*, blue with red, green or blue with yellow. (2) The acid colour should be run into a solution of the basic dye-stuff. (3) Quick judgment is necessary to determine the end point. A good method is to note the appearance of a ring of the colour of the reagent in a spot of the liquid on filter paper.

Brown and *Jordan* have shown that the method can be usefully employed in the following cases:—Auramine, by direct titration with Indigo Carmine; Methyl Violet, with Naphthol Yellow S; and Victoria Blue B, with Tartrazine. In the case of most other basic dye-stuffs titration with an acid colour alone did not give a definite end point. In several cases a useful modification was titration with a solution containing tannic acid and sodium acetate in addition to the acid colour. Brilliant Green and Malachite Green were titrated with a solution containing 1 grm. Orange II.,

* *Chem. News*, 1881, lii., 7.
† *Journ. Soc. Chem. Ind.*, 1906, xxv., 735.
‡ *J. Soc. Dyers and Col.*, 1923.
§ *Monatsh. Chem.*, 1913, xxxiv., 255.

2 grms. tannic acid, and 2·5 grms. sodium acetate per litre. Magenta and safranine were estimated by a similar method with indigo carmine in place of orange II., and rhodamine with Metanil Yellow and the tannin addition. For Methylene Blue, Tartrazine, or Crystal Scarlet, in either case with tannin, might be employed.

With regard to acid colours, the process was the same, the volume of solution of acid dye-stuffs required to precipitate a given weight of basic colour being an index of the colour strength. Trustworthy valuations were only possible in the case of Orange I., Orange II., Tartrazine, and Naphthol Yellow S, and for all these dye-stuffs the reacting basic colour was Victoria Blue or Night Blue. Eosine could be estimated by running a solution of the dye-stuff into a Malachite-green solution.

With direct cotton colours, much less progress had been made. The method suggested by *Baenziger* and *Vlies*, for the estimation of Benzopurpurine 4 B with Methylene Blue, did not give a satisfactory end point, whichever dye-stuff was employed as precipitant. A better result was obtained by adding to the Benzopurpurine solution an excess of Victoria blue B and titrating back with Orange II. An alternative was the addition of excess of auramine, titrating back with Indigo Carmine, a method which also served for the valuation of Chrysophenine.

Titration with Hydrosulphite.—A method of estimating soluble azo dyes has been based by *Grandmougin* and *Havas** on the titration of a solution of the dye-stuff with a solution of sodium hydrosulphite (3 grms. per litre containing 5 c.c. of 30 per cent. sodium hydroxide solution). The titration is effected in very dilute hydrochloric acid solution in an apparatus from which air has been expelled by a current of hydrogen, and is continued until decolorisation takes place :—

$$R\,\mathrm{N:N}\,R' + 2\mathrm{Na_2SO_4} = R\,\mathrm{NH_2} + R'\mathrm{NH_2} + 4\mathrm{NaHSO_3}.$$

The amounts of hydrosulphite used are inversely proportional to the molecular weights of the dye-stuffs as is shown by the following examples :—

	c.c.	Mol. weight.
Orange II.,	28·0	350
Chrysoin,	31·0	316
Fast red,	24·5	400

* *Chem. Zeit.*, 1912, xxxvi., 1167.

CHAPTER VII.

EXAMINATION OF WRITING INKS.

THE number of substances entering into the composition of ink is very large; but since the influence of many of these on the permanence of the writing is unknown, a full analysis of an ink does not afford full information, and needs to be supplemented with the results of practical tests.

According to the Prussian Regulations of 1888 an ink for documentary purposes had to contain a certain minimum proportion of tannin or gallic acid derived from galls (*vide infra*). It was, however, shown conclusively by *Schluttig* and *Neumann*, who submitted samples of different inks to examination, that the chemical tests employed were quite incapable of identifying an ink prepared, *e.g.*, from chestnut bark, and they, therefore, contended that an ink prepared from tannin or gallic acid derived from any source should be permitted in inks of Class I.

Similar criticisms were made by *Hinrichsen* and others, and the result has been that when the Prussian Regulations were altered in 1912 no attempt was made to differentiate the possible sources of the tannic acid.

The requirements of a good ink are:—(1) It must yield permanent writing which becomes relatively black within the course of a few days; (2) it must flow readily from the pen, and penetrate well into the fibres of the paper, without passing right through the paper; (3) it must not gelatinise or become mouldy in the ink-pots; (4) it should have a minimum corrosive action upon steel pens; (5) the writing must not be sticky (except in the case of some copying inks).

FLUIDITY OF INK.—*Schluttig* and *Neumann* recommend their stripe test (p. 159) as a means of determining the capacity of an ink to flow readily from the pen without spreading too freely on the

paper. At the point where the glass pipette touches the paper in their test, an oval head to the stripe is formed, whilst the remainder of the stripe is nearly as wide. Of 81 inks examined by *Schluttig* and *Neumann*, the majority gave the same results as the typical ink, whilst the copying inks yielded somewhat narrower stripes. Inks flowing too readily, however, produced a much wider head, while the lower part of the stripe was contracted to a narrower band than the others.

We have found a simple viscometer, consisting of a 50 c.c. pipette to give concordant results when used in the following manner :—The pipette is standardised with distilled water at 15·5° C., the time required for the liquid to run down to a given mark on the lower stem being taken as *unity*. The ink is then brought to the same temperature, and the time taken for the same volume to run out determined in the same way. Thus, in a pipette from which the water ran out in 40 seconds, we found that different writing inks required from 42 to 55 seconds, whilst copying inks in some cases required 70 seconds.

PENETRATION THROUGH PAPER.—This is best determined by a practical test on standard paper, under the same conditions as used with the typical standard ink. The ink should penetrate into the fibres, but should not come through the paper.

STICKINESS OF WRITING.—Here, again, the best results are obtained by comparison with a typical ink, as recommended by *Schluttig* and *Neumann*.

COMPOSITION OF COMMERCIAL INKS.—The following table gives the results of partial analyses of certain well-known commercial inks. It will be seen that the blue-black inks of the three different manufacturers are very similar in character :—

Ink.	Specific gravity at 15·5° C.	Water.	Total solid matter.	Ash.	Iron.	Efflux viscosity (Water at 15·5° C. = 40 seconds).
		Per cent.	Per cent.	Per cent.	Per cent.	Seconds.
1. Blue-black I.	—	96.21	3.79	0.764	0.32	—
2. " I.	1.0206	96.42	3.58	0.767	0.32	52
3. " II.	1.0214	96.44	3.56	0.90	0.27	49
4. Chrome ink .	—	98.70	1.22	0.26	—	42
5. "Japan" ink .	1.0413	92.74	7.26	2.18	0.84	55
6. Blue-black III.	1.0141	97.44	2.56	0.58	0.23	43
7. Black ink (logwood) . .	1.0115	97.86	2.14	1.04	0.14	43

The following table gives other analyses made by the writer of the principal black and blue-black writing inks on the market in 1908:—*

Ink.	Specific gravity at 15° C.	Water per cent.	Total solids per cent.	Mineral matter (ash) per cent.	Iron per cent.
Arnold's Blue-black	1.0216	96.35	3.65	0.94	0.25
Blackwood's Blue-black	—	96.82	3.18	0.77	0.28
,, Record	—	92.06	9.94	1.40	0.59
Carr's Blue-black	1.0220	96.01	3.99	1.07	0.29
,, Black	1.0224	95.84	4.16	1.39	0.48
Day and Martin's Blue-black	—	92.25	7.75	2.52	1.09
Draper's "Dichroic"	—	95.16	4.84	1.10	trace
Faber's Blue-black	1.0205	95.58	4.42	1.22	0.49
Field's Black	1.0153	96.66	3.34	0.82	trace
,, "Non-corrosive"	1.0121	97.55	2.45	0.64	0.28
Halsey's Blue-black	1.0208	95.35	4.66	0.54	0.28
Lyon's Blue-black	1.0239	95.14	4.86	1.01	0.35
Mordan's "Azuryte"	—	95.94	4.06	0.86	0.29
,, Blue-black	1.0225	95.54	4.46	0.62	0.18
,, "Jet-black"	1.0256	94.04	5.96	0.99	0.21
Morrell's Blue-black	1.0276	95.16	4.84	1.66	0.56
Paul's Blue-black	—	96.12	3.88	0.97	0.33
,, Black	—	96.68	3.32	2.28	trace
Pridge's Blue-black	1.0499	92.22	7.88	1.88	0.84
,, Black	—	92.32	7.70	1.42	0.49
Stephen's Blue-black	1.0206	96.21	3.79	0.76	0.32
Vicker's "Penwing"	—	98.11	1.89	0.42	trace
Walkden's Blue-black	1.0221	95.58	4.42	0.72	0.22
,, Black	1.0293	94.39	5.61	1.12	0.36

These results show that, notwithstanding the probably closely similar methods of preparation, there are yet wide variations in the composition of the different inks. Thus the total amount of solid matter (dried at 100° C.) ranges from 1·89 to 7·94 per cent., the ash from 0·42 to 2·52 per cent., and the iron in the iron-gall inks from 0·18 to 1·09 per cent.

Since these analyses were made the writer has on several occasions examined samples of the same kinds of inks, and the results have shown that the composition of an individual preparation by the same manufacturers remains fairly constant.

A qualitative test that sometimes enables one to distinguish between inks of different makers is their behaviour on titration with a saturated solution of bromine water. Thus, the blue-black

* *Analyst*, 1908, xxxiii., 80.

ink I. became first dirty grey, and then greyish-black; whilst No. II. first changed to violet and became turbid brown on the further addition of the reagent; and No. III. first became violet and then dirty green, the liquid remaining clear all the time. This last ink was also characterised by the ash being very difficult to burn white, and being then extremely insoluble in hydrochloric acid.

The presence of logwood in an ink is readily identified by the colour changing to bright red on the addition of hydrochloric acid (see p. 124). When indigo is also present the hydrochloric acid gives a purple coloration.

Indigo increases the stability of an ink towards bleaching agents such as bromine water. An ordinary iron gall ink is rapidly decolorised on the addition of strong hydrochloric acid, but, if indigo is present, the liquid remains blue, even after being boiled with the reagent.

DIFFERENTIAL REACTIONS ON PAPER.—When a drop of ink is applied to thick filter paper a certain amount of separation of its constituents will take place owing to the different rate of diffusion, and on this fact *Schluttig* * has based a series of differential tests. This method of fractionation gives the best results if the ink is previously diluted with an equal volume of water (3 to 4 times the volume in the case of copying inks).

Iron-gall inks give a light brown outer zone which becomes blue on treatment with solutions of potassium bisulphate and potassium ferrocyanide. Inks from Chinese or small Asiatic galls, *Knoppern*, divi-divi, valonia, oak bark, chestnut bark, and logwood give, after one or two days, an outer zone which is either of light brown colour or tinted with the provisional colouring matter.

The inner zone will be blue-black and, in the case of inks made from galls and divi-divi, will show characteristic lines in the margin, which are not to be found in the case of inks made from tan barks or logwood.

Inks made from sumach, and especially myrobalans, show a dark-grey inner edge to the outer zone owing to the diffusion of the black iron tannate. In the case of myrobalan ink a blue-black line on which is a light-grey band is found between the two zones. Both are absent in the case of sumach inks, and the uniform blue-black inner zone is in direct contact with the yellowish-green outer zone.

Chrome logwood and logwood copying inks show, at most, a light grey outer zone, which is free from iron.

* *Lunge's Technical Analysis*, Eng. Ed., 1914, p. 519.

SCHLUTTIG AND NEUMANN'S STRIPE TEST.—For comparison in their colorimetric method, *Schluttig* and *Neumann* make use of a standard ink containing the following constituents:—Gallotannic acid, 23·4 grms.; gallic acid, 7·7 grms.; gum, 10 grms.; hydrochloric acid, 2·5 grms.; and ferrous sulphate, 30 grms. in a litre of water. After standing for not less than four days, this ink is decanted and kept in a well-corked bottle.

In testing an unknown ink, 10 to 15 c.c. are compared with the standard ink, and, should there be a difference in shade, a small quantity of one or more suitable aniline dye-stuffs is added to the standard, so as to make the colours match.

The apparatus required consists of a frame (Fig. 38) over which is tightly stretched a piece of standard writing paper. This frame is fixed at an angle of 45°, and the unknown ink is allowed to run down this from a special pipette delivering 0·6 c.c. and producing a stripe about 6 mm. wide and 270 mm. in length. A similar stain is made with the ink after dilution with an equal quantity of water, and also with the standard ink before and after dilution.

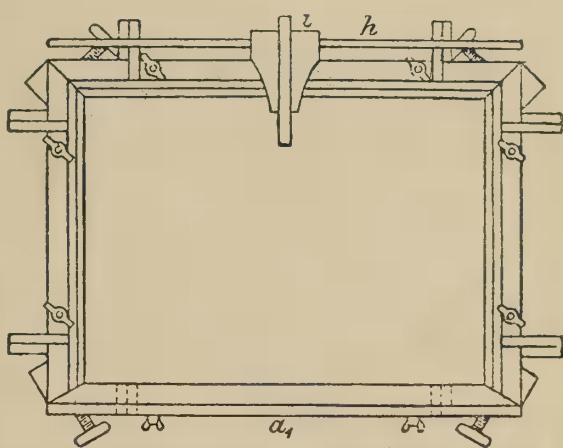


FIG. 38.—Schluttig's frame for stripe test.

The groove, *i*, at the top of the frame is intended as a rest for the pipette so that its point may always be applied at the same angle to the surface of the paper, and a channel is provided at the bottom to catch the excess of ink.

Provided the conditions are comparable, the stripes produced by different inks will vary in breadth and intensity with the fluidity of the ink and its degree of adhesion to the paper. In the case of copying inks the narrowness of the stripe affords an indication of the copying capacity.

When the ink is dry the paper is set aside in a place exposed to light and air, and after eight days the stains are compared with the standard stains with regard to their colour, while their shape also gives an idea of the fluidity of the original ink. The paper is also to be cut in strips horizontally and one piece immersed in water, another in alcohol of 85 per cent. strength, and a third in alcohol of 50 per cent. strength for several days. If the stripe of any particular ink

becomes paler than that of the typical ink under these conditions, *Schluttig* and *Neumann* conclude that the former is either too poor in gallic or tannic acid, or contains too much acid.

The objects of repeating the test after dilution are that the added aniline colours have less disturbing influence in the diluted ink, that differences of intensity are more pronounced, and that differences in the breadth of the stripes given by copying inks are reduced to a minimum.

Schluttig and *Neumann* do not contend that all inks must have the composition of their typical preparation, but assert that while containing at least 0·6 per cent. of iron, they must give equally satisfactory results in the different tests.

In place of the somewhat complicated apparatus devised by *Schluttig* and *Neumann*, we have found that sheets of Bristol board placed on a wooden stand fixed at an angle of 45° give satisfactory and concordant results in this test.

ACIDITY: ACTION ON STEEL PENS.—*The Function of Acid in Ink.*—The control of the acidity is one of the most important points in the manufacture of iron-gall inks, for it is the principal factor upon which the stability of the preparation depends. The writer has shown * that in the oxidation of ink in the so-called "drying" process there is a gradual change from a soluble ferrous tannate first into colloidal and then into insoluble tannates of iron, and that this oxidation may be accelerated by the presence of certain catalysts —*e.g.*, saliva. In the case of a mixture of a solution of ferrous sulphate and gall extract, or gallotannin, this change takes place fairly rapidly, and deposits and incrustations are formed in the liquid. By adding a certain proportion of strong acid, however, the oxidation process is arrested, and by a suitable regulation of the proportions of the mixture the ink is retained in the form of a stable solution or colloidal suspension until, when applied to the paper, the proportions become so altered by evaporation that the successive changes into the final insoluble resinous iron tannate take place.

Amount of Added Acid in Ink.—It is essential that the quantity of acid added should be kept within definite limits. If too little is added the ink will not acquire the desired stability, whilst if the amount is materially exceeded the ink will have an excessive corrosive action upon steel pens, and the dyestuff used as a provisional colour may even be bleached.

Inkmakers have gradually learned by experience to know the permissible variations of the acidity of their products, but unless this factor is chemically controlled unexpected troubles may occur.

* *Analyst*, 1920, xlv., 247.

The acids commonly used as stabilising agents are sulphuric, hydrochloric, and oxalic acids, preference being usually given to hydrochloric acid. In the German standard ink 2·5 parts of hydrogen chloride are added to 1,000 parts of ink. This formula has also been adopted for use as a comparative standard in the United States specifications for writing ink.* The British Government specifications, which were issued about four years ago, fix standards for the proportion of iron, but no reference is made to the acidity of the inks.

Inks without Added Acid.—Several manufacturers prepare an ink to which no addition of strong acid is made. These consists essentially of iron gallate or of a complex iron gallate, for solutions of such salts when exposed to the air do not undergo the changes to which solution of ferrous tannate are liable. A solution of gallic acid and ferrous sulphate is practically stable under conditions that will cause a solution of gallotannin and ferrous sulphate to yield deposits and incrustations. For example, the writer exposed a solution of 3 grms. of gallic acid and 2 grms. of ferrous sulphate to the air for thirty-five days and only obtained a deposit of 0·036 grm., and the filtrate, on further exposure for weeks, yielded only a slight trace of deposit.

Hence a gallic acid ink has the advantage over an iron-gall ink of not requiring the addition of acid, and so of having little, if any, corrosive action upon a steel pen, although this point is not of importance in the case of fountain-pen inks, which are intended to be used with pen-nibs not attacked by dilute acid.

On the other hand, the general opinion of practical inkmakers is that gallic acid inks lack " body " and do not penetrate the fibres of the paper so readily as acidified gallotannic inks. The low proportion of solid matter in some of these inks is attributable to the small solubility of gallic acid in water (about 0·5 per cent. at 15° C.), which also limits the proportion of iron which can be introduced into the ink. Some of the oxyferrigallates are more soluble than ferrous gallate, but it is questionable whether it would be possible to prepare a standard ink containing the 0·5 per cent. of iron required by the British Government specifications solely by the use of gallic acid.

The other question of the alleged inferiority in penetrating power of gallic acid inks could probably be definitely decided by comparative microtome tests.

The final composition of the inks depends to a considerable extent upon the copperas used in the manufacture, and variations in this salt may also have an influence on the acidity (see p. 107).

* *cf. Analyst*, 1921, xlvi., 61.

Estimation of Strong Acid in Ink.—The presence of the blue dyestuff used as provisional colouring matter renders direct titration of ink very uncertain. Electrometric titration would probably give satisfactory results, but the conditions would have to be worked out for each kind of ink. That is to say, the conditions for a hydrochloric acid ink would differ from those required by an oxalic acid ink, and in every case a method would have to be devised to distinguish between the strong acids and the weak organic acids in ink.

The only method hitherto adopted for estimating strong acids in ink is the somewhat crude one of immersing a weighed pen nib in a measured quantity of the ink, and estimating the amount of metal dissolved. This method, which the writer devised some years ago and published in the first edition of this book, has recently been included in the United States specifications (*supra*) without acknowledgment.

In one experiment in which a steel pen was immersed in 10 c.c. of a well-known blue-black ink the pen lost 5·18 per cent. in weight in a month, while the ink itself had become nearly solid.

It is thus evident that the contention of *Schluttig* and *Neumann* * that free acid does not act upon metals in the presence of tannin is not justified by the results of experiments.

Schluttig and *Neumann* consider that it is not possible to fix a maximum amount of acidity. They recommend their stripe test as the best means of determining whether too much acid is present, since ink darkens more slowly the greater the proportion of acid. Thus, if the stripes are as intense a black in as short a time as those given by their standard ink, they consider the amount of acid as not too great.

Rupert † has attempted to remove some of the objections to this test by standardising it as far as is possible. He uses pens of unplated steel and of the same size and manufacture, and takes the average of five separate tests with such ink. The pens are washed successively with alcohol and ether and weighed, and one is put into 10 or 20 c.c. of each of the samples of ink, and then left for seven days in loosely covered bottles, after which they are wiped, dried, and weighed.

Mechanical Tester.—For testing inks under nearly working conditions a device is used which dips the pen at intervals into the ink and allows it to dry between the immersions. An apparatus of the kind is shown in the diagram (Fig. 39), in which the clock has a circular plate with four equidistant projections attached to the minute hand shaft, and there is a spring which makes

* *Loc. cit.*

† *J. Ind. Eng. Chem.*, 1923, xv., 489.

contact for a few seconds with each projection as it is carried round. The motive force is supplied by a dry cell and a 2-spool electro-magnet of suitable strength and resistance; there is also an aluminium bar, 10 inches long, pivoted at one end so as to move vertically, an armature at the middle of the bar just over the magnet, a cross bar at the other end to support the pens, and a brass spring (or rubber band) to raise the bar when released.

Four pen nibs can be supported from the bar and from the cross-bar by means of iron wires passing through holes in the bars and through slots in the pens. The ink is contained in four small jars each holding about 20 c.c.; when contact is made the nibs are practically completely immersed, and they are just out of the ink when the bar is released. A test of five to seven days is sufficient for the purpose, and the appearance of the pen after it has been used for a day or two longer enables an estimate to be formed of the amount of deposition.

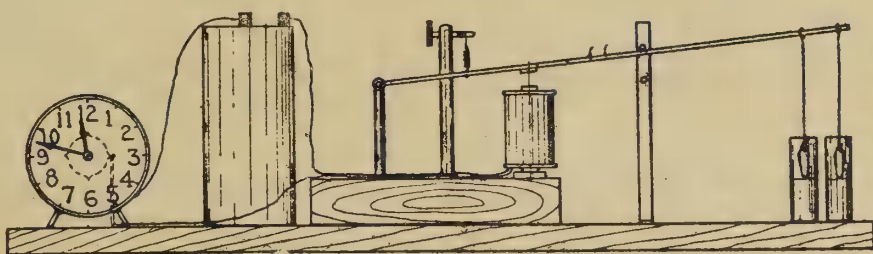


FIG. 39.—Mechanical ink tester.

Distillation with Sodium Acetate.—A much more accurate and rapid method of estimating the corrosive acids in ink is the distillation method devised by the writer.* This consists in distilling 10 c.c. of the ink with an excess of a neutral solution of sodium acetate and titrating the acetic acid in the distillate.

The objection to the process is that it requires at least three distillations of portions of 100 c.c. each to expel practically the whole of the acetic acid, for *Leeds* † and subsequently *Brode* and *Lange* ‡ have shown that traces of free acetic acid are obstinately retained by organic matter. Distillation with xylene as a carrier, as suggested by *Pickett* § does not offer any advantage in this case.

Estimation of Total Acidity.—A satisfactory method of estimating both the added acid and the weak organic acids is to bleach the pigments with hydrogen peroxide as follows:—Five c.c. of the ink are boiled for a few minutes with 10 c.c. of the ordinary 10 vol. hydrogen peroxide solution beneath a reflux condenser, the flask

* *Analyst*, 1921, xlvi., 131.
† *Ibid.*, 1895, xx., 224.
‡ *Ibid.*, 1909, xxxiv., 157.
§ *J. Ind. Eng. Chem.*, 1920, xii., 570.

being continually shaken until a pale straw-coloured solution is obtained. This is cooled, diluted with three or four times its volume of water, and titrated with *N*-alkali solution, with phenolphthalein as indicator. A blank test is also made with 10 c.c. of hydrogen peroxide diluted with 10 c.c. of water, and the acidity deducted from the previous result.

The writer has proved by experiment that the hydrogen peroxide treatment does not oxidise any constituents of gall extract into acids, which would otherwise increase the acidity of the ink.

Application of the Method to Logwood Inks.—Hæmatoxylin, the colouring matter of logwood, is not bleached when boiled with hydrogen peroxide, and the method is therefore not directly applicable to logwood inks. Hence, in the case of such inks it is necessary to use the following modification of the method:—Five c.c. of the ink are boiled with 20 c.c. of hydrogen peroxide solution and 2 c.c. of *N*-sodium hydroxide solution for about five minutes, until the liquid becomes transparent and pale. It is then cooled, diluted with a large volume (five or six times) of water, and the excess of alkali titrated with standard sulphuric acid, with Congo red as indicator (litmus or phenolphthalein being bleached). As before, a blank test is made to determine the correction to be applied for the acidity of the hydrogen peroxide.

No acids are formed when hæmatoxylin is boiled with the alkaline hydrogen peroxide, and sulphuric acid added to such a solution can be accounted for quantitatively after the treatment. In the case of Antoine's ink (No. 1 in the table), which is a logwood ink, it is interesting to note that the total acidity estimated by the hydrogen peroxide method is very slightly lower than the acidity due to strong acids, as found by the distillation method.

Acidity Control of the Manufacturing Process.—The hydrogen peroxide method affords a simple method of controlling the correctness of the manufacturing process. For example, in the case of an ordinary iron gall or gallic acid ink prepared by a specified formula the total acidity remains fairly constant from month to month. Any pronounced variation from this figure will point either to some deviation from the formula, or to the action of some external influence.

In 1920 complaints were received by different manufacturers of ink of the occurrence of the deposits in the bottles, and in some of the worst cases the ink itself had faded. The composition of the ink was in most cases normal, with the exception of the acidity being somewhat lower than usual, and it therefore appeared as though the ink had been sent out insufficiently matured, so that a

deposit which should have formed in the vats had formed in the bottles.

In one case, however, the total acidity estimated by the peroxide method was only 1·5 c.c., or rather less than half the normal value. It was then discovered that it was not the ink, but the glass of the bottle which was at fault.

Acidity of Commercial Inks.—The following results were obtained by means of the methods described with representative samples of commercial inks, the results in each case being expressed in terms of c.c. of *N*-alkali neutralised by 10 c.c. of ink :—

Ink.	Total Acidity.	Strong Acids.	Weak Acids.
	c.c.	c.c.	c.c.
1. Antoine, violet black, . .	1·60	1·76	nil
2. Arnold, blue-black, . . .	1·93	0·30	1·63
3. Blackwood, "Record," . .	5·62	1·55	4·07
4. Cochran's blue-black (1912) (heavy deposit).	1·93	0·60	1·33
5. ,, acid-free ink, . .	3·10	0·01	3·09
6. Field's blue-black, old, . .	2·66	..	..
7. ,, ,, new, . .	2·99	0·17	2·82
8. Hollidge, blue-black (heavy deposit),	7·0	0·40	6·60
9. Mordan's "Azuryte," . .	4·06	0·98	3·08
10. Morrell's blue-black (faded, heavy deposit).	1·92	0·07	1·85
11. Stephen's blue-black, . . .	3·83	2·46	1·37
12. "Swan,"	3·42	1·82	1·60
13. Typical blue-black ink (deposit), April.	3·20	..	..
(*a*) ,, (faded), August, .	0·15	..	..
(*b*) ,, (alkaline), January,	−0·30	nil	..
14. Tarling, blue-black, . . .	3·85	1·35	2·50
15. Webster "Diamine ink" (old, heavy deposit).	0·48	0·08	0·40
16. ,, ,, (new), .	3·68	0·18	3·50

Influence of Alkaline Glass on the Acidity of ink.—When cold distilled water was placed in the empty bottles, after thorough cleaning, or when the bottles were immersed in water, alkali was rapidly dissolved, and, after about five minutes, the water showed a pronounced alkaline reaction towards phenolphthalein.

Two series of tests were made with two new bottles of the same consignment. Each was filled with water, and 10 c.c. portions were titrated with *N*-sulphuric acid at subsequent periods, with the

following results:—I. After 4 hours, 0·47 c.c.; after 24 hours, 0·94 c.c.; after 48 hours, 0·94 c.c.; after 72 hours, 0·94 c.c.; and after 9 days, 0·47 c.c. II. After 3 days, 0·71 c.c.; 13 days, 0·75 c.c.; 20 days, 0·66 c.c.; and 24 days, 0·14 c.c.

It appeared therefore, that the reaction was retrogressive, the alkali first liberated by the water from the sodium silicate or the alkali carbonate dissolved again entering into combination with other constituents of the glass.

An analogous test was made by placing 18·9 c.c. of *N*-sulphuric acid in bottle No. 1. After eleven days the acidity had fallen to 12·8 c.c.

The same effect is produced by ink, as is seen by the results given by the sample No. 13, in which the change was followed from an acidity of 3·2 c.c. to a alkalinity of 0·30 c.c.

Nor does ink free from added acid fare any better when placed in these bottles. For instance, a sample from a bottle of Field's ink, the bulk of which was still quite free from any deposit, produced a thick incrustation on the sides of one of the bottles within three days, whilst its total acidity, as determined by the hydrogen peroxide method, fell from 2·99 c.c. to 0·35 c.c. in sixty days, and the colour changed from bright blue to brownish-purple.

It is quite possible that the cheaper kinds of glass bottles, such as are used for ink, may not infrequently yield a considerable proportion of free alkali to any liquid placed in them, and that this may be the hitherto unsuspected reason for the occasional deterioration of ink in bottle.

This was borne out by an experiment with the bottle which had contained the faded, decomposed Morrell's ink (No. 10). After thorough washing, the bottle was filled with distilled water, and the liquid tested daily. For five days it remained neutral to phenolphthalein, but on the sixth day gave a very faint pink coloration, and on the seventh day a distinct alkaline reaction. Hence, although this glass was much less alkaline than that of the bottles mentioned, it seems reasonable to conclude that in this instance, also, it was the cause of the instability of the ink.

The glass of the very alkaline bottles was distinctly vitreous in character, but this less alkaline glass was much clearer, and it is possible that a relationship might be established between the alkalinity and the transparency of glass.

STABILITY ON KEEPING.—A good ink will frequently keep as long as a year without throwing down any insoluble deposit on the sides of a vessel, provided air be excluded. At the same time, if a sample bottle contain some deposit, the ink is not necessarily of bad

quality, since this may be due to changes of temperature. Should there be a pellicle, however, in a sample bottle, the ink should be rejected as inferior.

Schluttig and *Neumann* have devised the following test for determining the stability of an ink in a comparatively short time:—The bottle containing the ink is allowed to stand for three days at a temperature of 10° to 15° C., after which 50 c.c. are withdrawn from the centre by means of a pipette without shaking the contents. This is filtered and 25 c.c. of the filtrate placed in a cylindrical glass vessel about 185 mm. high and 72 mm. in diameter, the mouth of which is then covered with paper to exclude dust.

Schluttig and *Neumann's* typical ink when thus tested remained unchanged for three weeks, after which a pellicle began to form on the surface, and small flecks to separate. This ink was obviously purer than ordinary commercial inks, many of which, however, remained unchanged for fourteen days or longer, and in *Schluttig* and *Neumann's* opinion this period should be fixed as the minimum keeping time for an ink of the first class under these conditions.

Detection and Estimation of Constituents.

ASH.—This is estimated by evaporating 10 c.c. of the ink and igniting the residue at a low temperature. Certain inks differ considerably from others in the readiness with which the carbon can be burned off. The cautious addition of a few crystals of ammonium nitrate facilitates the ignition.

IRON.—The ash is dissolved in hydrochloric acid, the solution oxidised with nitric acid, and the iron precipitated with ammonia. Or the volumetric method described on p. 169 may be used.

CHROMIUM.—The ash is fused with sodium carbonate, potassium nitrate, and potassium hydroxide, the mass dissolved in water, acidified with acetic acid, filtered, and the chromate precipitated as lead chromate.

GUMS AND DEXTRIN.—Ten c.c. of the ink are treated with twice the volume of 95 per cent. alcohol, and the precipitate collected on counterpoised filters, and dried and weighed.

Malagnini gives the following method of distinguishing between dextrin and gum:—The ink is diluted, treated with basic lead acetate and saturated with hydrogen sulphide, the excess of which is removed by boiling. The presence of sucrose or dextrose may then be detected in the filtrate.

Dextrin is detected by giving a precipitate in white flakes on the

addition of a large excess of alcohol. The precipitate when dissolved in water shows a strong dextro-rotation.

Gum is detected by acidifying the ink with strong hydrochloric acid, and adding much alcohol. Any precipitate is washed with alcohol and treated with strong hydrochloric acid. The liquid is divided into two portions. One of these is boiled with phloroglucinol, and in the presence of gum gives a rose-violet coloration. The other portion is boiled and treated with a few drops of aniline, which in the presence of gum gives the furfural reaction (rose-red coloration).

GLYCERIN.—The total solids of the ink are treated with strong alcohol (96 per cent.) the alcoholic extract evaporated, and the residue tested for glycerin. If glycerin is present, fumes of acrolein will be liberated on heating with potassium bisulphate, ; *Schiff's* reagent (magenta decolorised with sulphur dioxide) will have its colour restored; and a blue coloration will be obtained with a 1 per cent. solution of sodium nitroprusside to which a few drops of piperidine have been added.

PHENOL AND SALICYLIC ACID.—The residue from the ink is mixed with sand, and extracted with ether. On evaporating the ethereal extract phenol may be detected by its odour and by giving a precipitate of tribromophenol with bromine water. Salicylic acid is readily recognised by the violet coloration given with a dilute solution of ferric chloride.

DYE-STUFFS.—A little of the ink is diluted, slightly acidified with hydrochloric acid, and boiled for 15 minutes with a thread of wool or cotton, while at the same time a parallel test is made with the ink after being diluted and made alkaline with ammonia. The threads are then thoroughly washed with hot water, and if they have been dyed they are boiled in sodium carbonate solution or acidulated water, again fixed on cotton or wool, and identified (see p. 146).

INDIGO CARMINE is fixed upon wool in an acid bath and redissolved by an alkaline bath. In alkaline solution it remains bright blue after the addition of sulphuric acid, but is changed to green by hydrochloric acid. With stannous chloride and hydrochloric acid it is decolorised by heating, but regains its colour when oxidised with a few drops of ferric chloride solution. It gives a yellow coloration with nitric acid or with chlorine water.

A colorimetric estimation of indigo carmine may be made by acidifying 1 c.c. of the ink with sulphuric acid and comparing the colour with that given under similar conditions by a standard solution of indigo carmine.

See also *Coloured Writing Inks*, Chap. vi., and *Printing Inks*.

Testing.

*Prussian Regulations for Official Tests of Ink.**

According to the Prussian regulations of May 22, 1912, inks are classified into (1) "documentary" and (2) "writing inks," the latter being subdivided into (*a*) iron-gall inks and (*b*) logwood and dye-stuff inks.

(1) "*Documentary ink*" is defined as an iron-gall ink which gives dark writing after eight days' exposure to light and air. It must contain at least 27 grms. of anhydrous gallotannic and gallic acids and 4 grms. of iron (calculated upon the metal) per litre. On the other hand, the amount of iron must not exceed 6 grms., so that the ratio of gallotannic and gallic acids to iron must lie within the limits 4·5 : 1 and 6·75 : 1. The ink must not alter for at least fourteen days in the ink-pot, and must flow readily from the pen. The writing done with it must not be sticky immediately after drying, and after eight days it must remain deep black when washed with water and with alcohol (85 and 50 per cent.).

(2) *Iron gall* "*writing inks*" (*a*) must contain at least 18 grms. of gallotannic and gallic acids, and at least 2·6 and not more than 4 grms. of iron per litre (ratio 4·5 : 1 and 6·75 : 1). In other respects they must comply with the requirements of "documentary" inks. Inks of Group B are not officially tested.

Analysis of Inks.—The proportion of gallotannic and gallic acids is determined by shaking the sample with ethyl acetate and weighing the residue left on evaporating the extract. The residue is regarded as gallotannic and gallic acids when 0·1 grm. thereof absorbs, in the presence of 2 grms. of sodium bicarbonate, at least 0·5 grm. of iodine. If less iodine is consumed the ink is not up to the official requirements.

Estimation of Gallotannic and Gallic Acids.—Ten c.c. of the ink are mixed with 10 c.c. of concentrated hydrochloric acid, and the mixture shaken with successive portions of 50 c.c. of ethyl acetate in Rothe's shaking apparatus, until the aqueous layer gives no reaction for gallotannic or gallic acids after treatment with sodium carbonate and addition of ferric chloride and ferrous sulphate. The ethyl acetate extract is shaken several times with semi-saturated potassium chloride solution (10 c.c. each time) to remove iron salts and then evaporated *in vacuo,* and the residue is taken up with a little water, transferred to a weighed crucible, and dried at 105° to 110° C. or, preferably, *in vacuo* at about 60° C. until constant in weight.

In determining the iodine absorption about 0·1 grm. of the residue is mixed in a stoppered flask with 2 grms. of sodium bicarbonate and 25 to 50 c.c. of a solution of iodine (about 50 grms. per litre), and the flask closed and allowed to stand over-night, after which the unabsorbed iodine is titrated with standard thiosulphate solution. Simultaneously a blank determination is made.

Iron.—Ten c.c. of the ink are evaporated to dryness, and the residue ignited until free from carbon and then heated with 1 to 2 c.c. of hydrochloric acid (sp. gr. 1·124) until dissolved. The solution is treated with 1 to 2 c.c. of chlorine water and evaporated to dryness, the residue treated with 0·5 c.c. of strong hydrochloric acid to dissolve basic iron salts, and the solution cooled and diluted with 20 c.c. of water. About 1 grm. of potassium iodide is then added, and the separated iodine titrated with $N/10$ thiosulphate solution,

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* Hinrichsen, *Chem. Zeit.*, 1913, xxxvii., 265.

the liquid being meanwhile rapidly warmed to 55° C. to promote the separation of iodine.

Testing the Writing.—Pieces of standard paper are stretched in a frame inclined at an angle of 45°, and a definite amount of ink made to flow down them from a pipette fixed in a special position with regard to the paper. At the same time a parallel test is made upon the same papers with Schluttig and Neumann's standard iron-gall ink containing 23·4 grms. of gallotannic acid, 7·7 grms. of crystalline gallic acid, 30·0 grms. of ferrous sulphate, 10·0 grms. of gum arabic, 2·5 grms. of hydrochloric acid, and 1·0 grm. of carbolic acid per litre. This ink is allowed to stand for at least four days at 10° to 15° C., and decanted from any deposit.

For comparison in the test it is coloured with a suitable dye-stuff to match the ink under examination. The paper with the colour strips of the two inks upon it is exposed to the air for eight days in diffused daylight, and is then cut horizontally into strips which are immersed in water, 50 per cent. alcohol and 80 per cent. alcohol respectively. No perceptible bleaching of the ink should take place.

Examination of Handwriting.

THE FADING OF INK IN WRITING.—*Acidity in the Paper.*—The fading of the writing in certain documents has been found to be due to free acid in the paper. To determine this factor *Vandevelde* * macerates 10 grms. of the paper with 100 c.c. of water for 24 hours, strains off the liquid and titrates the filtrate and washings with $N/10$ alkali. The acid coefficient thus found should not exceed 50. In various samples of paper thus tested it ranged from 0 to 280.

Atmospheric Influences.—The rate of fading of an ink will depend upon the influence of gases in the air under the conditions to which the writing is subjected. If, for instance, it is exposed in the vicinity of chemical works it will fade more rapidily than in normal air, and the particular constituents of which it is composed will also affect the results. Light and moisture will also promote the chemical changes.

For the measurement of changes taking place in pigments on exposure, *Lovibond* † recommends the use of his tintometer (*cf.* p. 180), and classifies colouring matters into the following groups in accordance with their behaviour when exposed under standard conditions : (1) Stable colours ; (2) Those increasing in density for a time ; (3) Those in which one factor increases while the other fades ; (4) Those in which all factors fade ; and (5) Those which after temporary changes revert to normal conditions of permanency.

OLD MANUSCRIPTS.—We have already pointed out that, although in many ancient manuscripts the writing is as distinct as

* *Journ. Soc. Chem. Ind.*, 1907, xxvi., 548. † *Ibid.*, 1905, xxiv., 262.

when first written, there are also numerous cases in which the characters have faded to such an extent as to be almost illegible.

Numerous methods have been suggested for restoring the intensity of the original writing, but many of these are open to the objection that they injure the surface of the material.

The oldest and best known of these methods was to sponge the writing with an infusion of galls, the tannin of which would once more combine with the iron left in the paper, thus forming a fresh ink. This method was described in the book of *Canneparius* in 1660.

A much more reliable method was that first proposed by *Blagden* in 1787, which was based on the formation of a blue compound by the action of a solution of potassium ferrocyanide and dilute hydrochloric acid on the residual iron in the paper. This affords an easy means of distinguishing between carbon inks and iron gall inks, and *Blagden* was thus able to show that the writing on certain vellum manuscripts of the ninth and fifteenth centuries consisted of iron ink, or of an ink which contained iron (see p. 9).

Lehner's method of applying this process of restoration is to immerse the paper for a few seconds in one per cent. pure hydrochloric acid, and to allow it to dry spontaneously. The writing is then dusted over with powdered potassium ferrocyanide, and covered with a glass plate on which is placed a weight. After being left for a few hours the paper is thoroughly dried, and the excess of ferrocyanide removed by means of a soft brush.

A more modern and less drastic method is to use a solution of ammonium hydrosulphide, which is applied for a few seconds until the writing becomes darker, and is then sponged off as rapidly as possible after the desired effect is obtained.

In this method the basic ferric salt into which the ink in the paper had decomposed is converted into the black ferrous sulphide. Writing thus restored may speedily be reoxidised so as nearly to disappear again, and the method can only be regarded as a temporary expedient. *Lehner* * has devised the following means of keeping writing thus restored for a longer period:—The damped paper is supported on a frame of threads fixed half way up in a shallow box (4 inches deep), whilst ammonium sulphide is placed in a small dish beneath. The box is closed by a glass cover, and after a short time the vapours of ammonium sulphide act on the writing, which becomes first brown and then black, and retains its intensity so long as the manuscript is left in the box.

PALIMPSESTS.—The name *palimpsest* is derived from the Greek words παλιν = again, and πσεστος = rubbed. It is applied to old

* *Die Tinten Fabrikation*, p. 144.

manuscripts, the parchment of which had been previously used for a similar purpose. This practice was doubtless due to the cost of new material. The first writing on the skins was obliterated by means of pumice or some other abrading substance, but the mechanical action was insufficient to remove characters, possibly written three or four centuries earlier. In cases where the iron constituent of the ink had sunk deeply into the vellum, it would be almost impossible completely to eliminate it, and the use of the reagents described above would reveal the original characters.

An interesting discovery of a palimpsest was that made in 1816 by Niebuhr, who found the lost classic, the "Institute of Gaius," concealed beneath some writings of St. Jerome in the Chapter House of the Cathedral at Verona.

Morides' Process.—This consists of softening the skin by leaving it in distilled water, then treating it with a one per cent. solution of oxalic acid to bring the residual iron in the paper into a soluble state, again rinsing it in water and immersing it in a one per cent. solution of gallic acid, which will again form ink with the iron. Finally, the parchment is washed in water and pressed between blotting paper. Care must be taken to avoid an excess of oxalic acid, which might completely destroy the writing, and the method has the further drawback that the parchment is sometimes blackened all over by the gallic acid.

Lehner advocates exposing the parchment to steam and then to acetic acid vapours before applying the gallic acid.

Potassium thiocyanate could also be used as a reagent, or the parchment might be moistened and exposed to the vapours of ammonium sulphide or of thiocyanic acid (potassium thiocyanate acidified with hydrochloric acid).

The vapour of hydrogen peroxide has been found an admirable reagent for restoring the original whiteness of water colour drawings in which white lead has been used as the pigment.*

It may also be noted that photography affords a ready and most efficient means of deciphering such partially obliterated writing, the pale yellow colour of the iron oxide from the old ink appearing black in a photographic copy.

Pringsheim and *Gradeviss* † have devised a method of intensifying the appearance of the older writing on a palimpsest, while reducing that of the newer writing. Two coinciding photographic negatives, A and B, are made from the parchment, but of different intensity. On the first the old writing is brought out as strongly

* *Bull.* No. 5, *Dept. Scientific and Industrial Research; Analyst*, 1922, 47, 120.
† *Muspratt's Handbuch Techn. Chem.*, 1905, viii., 1397.

as possible, while the new writing is made as faint as possible. On the second writing the two writings are rendered about equally intense. A glass positive is then prepared from this second negative and is superposed on the first negative so that the lines coincide. On now examining them by transmitted light, the surface of the parchment (strong in the negative and faint in the positive) and the newer writing (faint in the negative and strong in the positive) will neutralise each other, while the older writing (strong in both negative and positive) will be rendered much more visible.

WRITING ON CHARRED PAPER.—*Habermann* * has devised methods of rendering the writing visible upon paper which has been charred, though not to the extent of leaving a white ash.

In most cases writing in iron-gall ink leaves a deposit of iron oxide which is still visible after incineration of the paper—but many printing inks disappear entirely. Others containing Prussian blue are plainly visible.

Pencil marks from ordinary graphite are nearly always visible, provided the heat of incineration has not been excessive. Red pencil marks are burned away, but blue marks persist owing to the presence of iron in the pigment.

In cases where the ash is not sufficiently coherent the following method is suggested: the carbonised fragments are painted on the side that is free from writing with a 10 per cent. solution of aluminium acetate or with the "fixing-fluid" (containing magnesium and thorium nitrates) used for gas mantles. They are then dried and gently ignited, so as to leave a white coherent ash. In the case of pencil marks there is some risk of burning off the graphite if nitrates be used, and aluminium acetate is therefore preferable for the strengthening, although it gives a less coherent ash.

A photographic method of deciphering writing or printing on charred documents has been devised by Davis.† The paper is attached, face downwards, to the emulsion side of a photographic plate, which is left in the dark for a week or two, after which it is developed in the usual way. The ink in the written or printed characters appears to act as a screen to protect the plate from gaseous products in the charred paper, which fog the plate. The result of the long exposure, therefore, is that the characters are shown in white on a black background on the developed plate.

A plate of fast or medium speed must be used, since slow plates

* *Zeit. anal. Chem.*, 1909, xlviii., 729.

† *U.S. Bureau of Standards, Sci. Papers*, 1922, xviii. (454), 445.

are not sufficiently sensitive, and a longer time of contact is required if the charred paper has been exposed to the air.

If films are used instead of plates, an exposure of two or three months is required and a positive result is obtained, the inked characters appearing black on a white background. By washing the films with water, however, and drying them before exposing them to the action of the charred paper, a negative result is obtained, as in the case of plates.

Forged Handwriting.

The police reports abundantly prove that the crime of forgery frequently engages the attention of our magistrates. This is not surprising when we remember that the means are in the hands of every one, and that bankers' cheques are a common medium of exchange. The usual evidence called by the prosecution is that of the handwriting expert, who bases his opinion on the form and peculiarities of the writing. We are inclined to think that much more stress might in many cases be laid upon the chemical aspect of the question. What we mean is that in a case where additional letters or figures have been added to, say, a banker's draft, it would be comparatively easy to ascertain whether the interpolated characters had or had not been written with the same ink as that used for the body of the document. When there is any objection to bringing chemical reagents in contact with the original paper, the camera can be employed in the way first brought into prominence by Dr. *Paul Jeserich*, which we describe at length in a subsequent page.

BLEACHING AGENTS.—It is possible to remove completely all traces of an ink stain (not containing carbon) by the use of suitable bleaching reagents, among which may be mentioned solutions of chlorine, bromine, acidified bleaching powder, etc.

Traill, in the course of his research into the permanence of inks, tested the affect of various reagents on the writing done with ordinary iron gall ink, and classified them into the following groups :—

I. *Those completely effacing the writing :—*

Solutions of chlorine ; chlorine of lime with weak acid ; antimony chloride ; dilute *aqua regia :* and oxalic acid.

II. *Those effacing the writing to a large extent :—*

Dilute nitric, sulphuric, and hydrochloric acids.

III. *Those rendering the writing faint :—*

Solutions of potassium and sodium hydroxides and ammonia.

To the first group we may add the following substances :—Bromine,

Reagent.	Iron gall ink.	Logwood ink.		Nigrosine ink.	Vanadium ink.	Resorcin ink.
		Potassium chromate.	Copper sulphate.			
Oxalic acid, 3 °/。	Bleached.	Violet.	Orange-yellow.	Unchanged	Smudged and bleached.	Bright red.
Citric acid, 10 °/。	Do.	Do.	Do.	Dark blue, smudged.	Do.	Bleached.
Hydrochloric acid, 10 °/。	Faint yellow stain.	Purple red.	Blood red.	Hardly altered.	Slightly bleached, smudged.	Bright rose.
Sulphuric acid, 20 °/。	Bleached.	Red.	Purple red.	Unaltered.	Slightly bleached.	„ red.
Nitric acid, 20 °/。	Do.	Do.	Do.	Slightly smudged.	Do.	„ rose.
Stannous chloride, 1; HCl, 1; water, 10.	Do.	Do.	Red.	Unaltered.	Do.	Bleached.
Sulphur dioxide, saturated solution.	Do.	Violet grey.	Do.	Do.	Slightly bleached, smudged.	Do.
Gold chloride, 4 °/。	Slightly bleached.	Red brown.	Brown.	Do.	Do.	Brown, smudged.
Sodium thiosulphate, ammonia and water (1 + 1 + 10).	Dark red.	Unaltered.	Dark blue.	Dark violet, smudged.	Very smudged.	Brown.
Potassium ferrocyanide + HCl + water (1 + 1 + 10).	Blue.	Red.	Purple red.	Unaltered.	Unaltered.	Rose.
Sodium hydroxide, 4 °/。	Dark red.	Brown.	Dark red, smudged.	Dark violet, smudged.	Dirty brown, smudged.	Unaltered.
Chloride of lime, 2 °/。	Bleached.	Bleached.	Yellow stain left.	Brown.	Unaltered.	Brown.

sulphur dioxide, sodium nitrate with hydrochloric acid, and citric acid; whilst hydrogen peroxide solution and potassium bisulphate speedily render the writing very faint.

As has been already mentioned, the addition of indigo to iron-gall ink renders it much more resistant to the action of these reagents, and the presence of various aniline dyestuffs influences the course of the reaction.

DIFFERENTIATION OF WRITING DONE WITH DIFFERENT INKS.—If writing from various sources be subjected to a systematic series of tests, differences in that done with different inks, or even at different periods, will generally be observed. For instance, in the case of the reagents used by *Traill* (*supra*), fifty envelopes were tested, and the writing on no two of them gave identical results.

Robertson and *Hoffman** employed the following reagents for distinguishing between writing done with different kinds of ink. In each case a feather was dipped in the reagent and a note taken of any change occurring at the junction of the ink and paper.

In Fig. 40 we show the results of testing the writing done with different commercial inks with certain bleaching reagents.

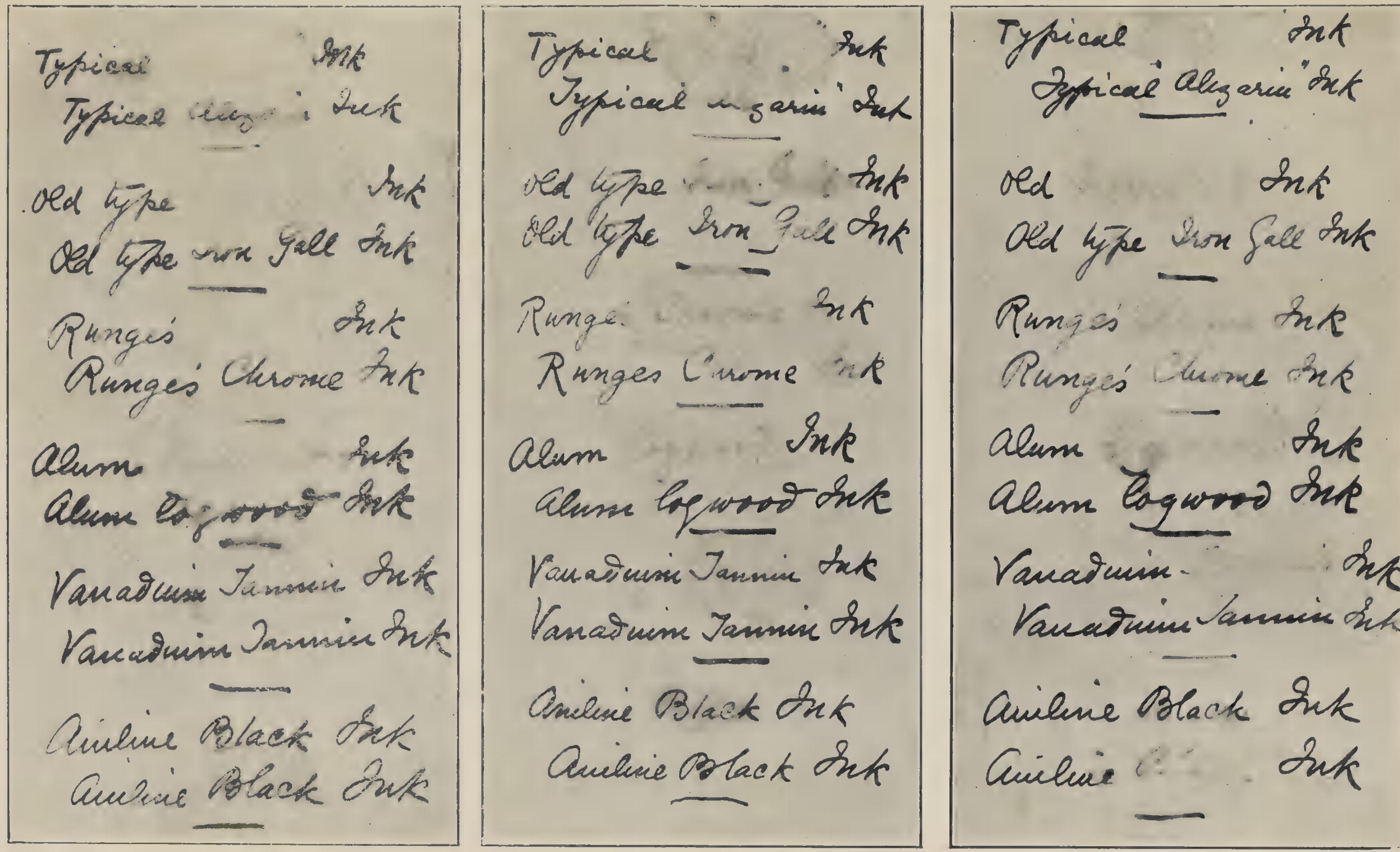
Obviously these tests can only be looked upon as typical examples, for numerous other substances are added to modern inks, and each of these may play a part in modifying the reaction given by any particular reagent.

The reagents that the writer has usually found sufficient for the differentiation of inks in writing are the following:—(1) Hydrochloric acid (5 per cent. solution); (2) Oxalic acid (5 per cent. solution); (3) Stannous chloride (10 per cent. solution); (4) Nascent hydrogen (50 per cent. HCl with zinc); (5) Bromine (saturated aqueous solution); (6) Bleaching powder (saturated solution); (7) Titanous chloride (commercial solution); (8) Potassium ferrocyanide (5 per cent. solution containing 1 per cent. of HCl).

Of these reagents the two first mainly act upon the iron tannate and leave the provisional colouring matter. The third and fourth bleach the iron tannate, and reduce the provisional pigment, changing its colour. The fifth and sixth reagents have an oxidising action upon both pigments, and cause more or less superficial bleaching. The titanous chloride solution is a powerful reducing agent towards both pigments, while the acidified ferrocyanide solution acts mainly upon the iron liberated from the iron tannate.

The reagents may be conveniently applied by means of a pipette, the end of which is drawn out to a capillary point, and the writing should be examined both by reflected and transmitted light, first

* Elsner, *Die Praxis der Chemiker*, p. 598.



HYDROCHLORIC ACID. OXALIC ACID. BROMINE WATER.

FIG. 40.—ACTION OF BLEACHING REAGENTS ON WRITING.

after five minutes, and then after twelve hours' exposure to the air.

The colorations that appear on the wrong side of the paper are sometimes also very characteristic, especially in cases where there has been superficial bleaching. In using titanous chloride it is advisable to take up the excess of the reagent with blotting paper five minutes after its application to the paper.

By means of these eight reagents the writer was able to distinguish between all the inks mentioned in the preceding table, p. 157.*

As a rule the pigments used as provisional colouring matters offer much greater resistance than iron tannates to the action of chemical reagents, whereas they are much less stable than the iron tannates when exposed to the action of light and air.

For matching and recording the colorations obtained with the different reagents the colour microscope devised by *Osborn* (p. 179) will be found useful.

Or colour standards may be prepared in the manner mentioned on p. 178.

The presence of chromate in an ink may be detected by *van Eck's* † test with α-naphthylamine and tartaric acid, after destruction of the temporary colouring matter by an oxidising agent. Benzidine also gives a blue coloration with chromates.

For the detection of forgeries in documents *Chevallier* ‡ recommended the following systematic series of tests: (1) Examination of the surface of the paper with a magnifying glass; (2) treatment with distilled water; (3) with alcohol; (4) with blue and red litmus; and (5) with various chemical reagents.

i. The colour of the ink is noted and any irregularities in the edges of the characters. If there has been any mechanical treatment the paper may appear thinner in some places than in others.

ii. Water may be absorbed more rapidly by one part than another.

iii. The object of the alcohol test is to detect removal of the size in the treatment which removed the writing. The writing on the rubbed part spreads out more and penetrates into the paper. Skilful forgers have employed rosin and glue to restore the surface of the paper. To detect this the paper is first treated with hot water and then with alcohol.

iv. The moistened document is placed between sheets of blue or

* *Analyst*, 1908, xxxiii., 80.

† *Chem. Weekblad*, 1915, xii., 7.

‡ *Dingler's polyt. Journ.*, 1832, xliv., 131.

red litmus on which is placed a weight, and a note taken of any change in colour and whether it is uniform.

v. The writing is moistened and treated with various intensifying reagents such as gallic acid, potassium ferrocyanide, alkali sulphide, or hydrogen sulphide, the treatment being repeated after twenty-four hours. Sometimes prior writing appears after the lapse of ten to thirty days.

Chevallier and *Lassaigne** advocate the use of iodine vapour applied to the moistened paper, a blue spot appearing where the sizing has been erased, whilst the remainder of the surface becomes brown.

The spots are then best treated with sulphur dioxide solution, then with a 3 per cent. solution of hydrogen peroxide, and lastly with ammonia. After removal of the excess of the last reagent tannin may be used to render any characters darker and more visible.

Potassium fluoride does not act upon indigo or aniline blue; but if characters made with Prussian blue are moistened with the solution and steam passed over them, white flecks appear.

ESTIMATING THE AGE OF WRITING.—In some cases it is possible to form an approximate idea of the age of ink in writing, though it is rarely possible to speak definitely upon the point. The principles upon which any such conclusions must be based are firstly the colour of the ink and secondly the speed of reaction with certain chemicals.

The Colour.—When blue-black ink is freshly applied to the paper the provisional blue colour will predominate, and the ink will appear bright blue even to the naked eye. But the black iron tannate rapidly forms, and gradually masks the blue colour, so that the ink when examined under the microscope will appear of a deep violet shade. This change in colour of the ink proceeds fairly rapidly in the light, but more gradually in the dark, but in any case is usually complete in the course of, at the outside, a few months. Now if the ink upon a document, alleged to be, say, two or three years old is of a bright blue colour, and is found by a chemical test to be a blue-black iron-gall ink, the fact is at once highly suspicious. If, further, the ink is found to change colour and become more violet on exposure to light and air, there can be but little doubt that it is not as old as alleged, since it would have reached its maximum intensity long before then.

In order to obtain a standard of comparison it is necessary to have a record of the colour when first examined under the microscope. One method of taking this record is to prepare a series of

* Elsner, *loc. cit.*, p. 600.

colour stripes from aniline dyes, and to match the colour of the ink under the microscope against these standards.

Then, by again comparing the standards with the ink after it has been exposed to the air and light for several days, it is possible to ascertain whether any change in colour has taken place.

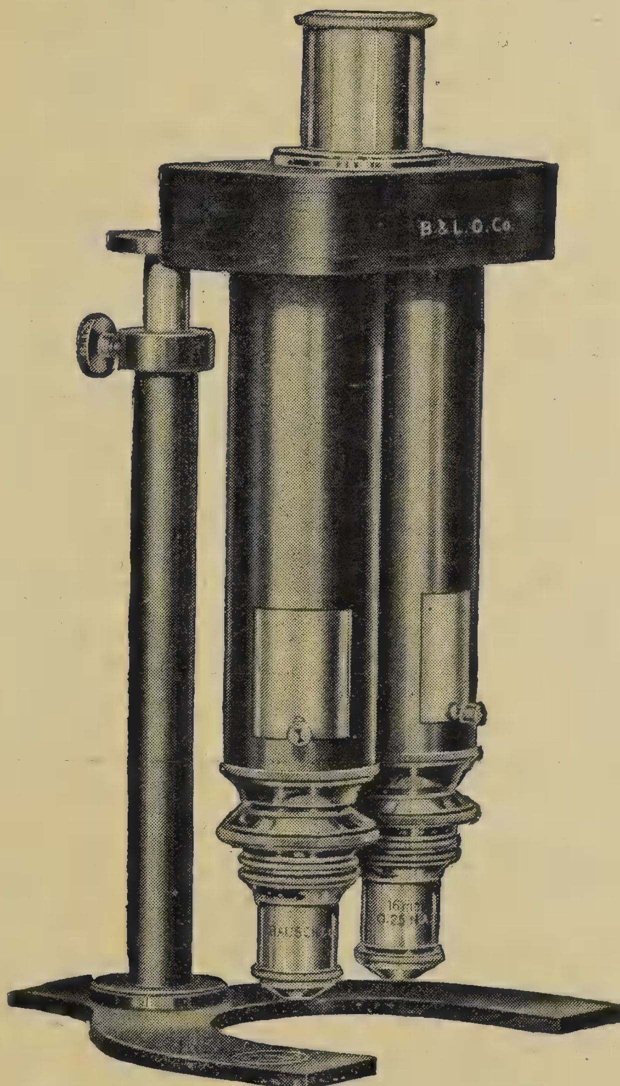


FIG. 41.—Colour comparison microscope.

This method has been successfully used by the writer in several cases, but it involves the use of a large number of standard stripes, and the colour comparison microscope invented by *Osborn* * obviates many of these difficulties.

THE COLOUR MICROSCOPE.—This ingenious adaptation of

* *Questioned Documents*, p. 361.

Lovibond's tintometer to the examination of inks under the microscope, shown in Fig. 41, is made by the Bausch and Lomb Optical Co. of Rochester, U.S.A. It consists of two distinct body tubes fitted into a prism box, in which is a double prism. The effect of this is to make each half of the field appear adjacent when viewed through the single eye-piece. In each of these tubes is a slot with sliding shutter intended for the introduction of the Lovibond standard glasses.

Days.	1			2			3			4		
	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.
Iron tannate,	0·9	0·3	..	1·0	0·5	..	1·3	0·6	..	2·0	0·8	0·2
blue-black ink,	3·0	..	..	3·75	0·5	0·3	4·0	0·7	0·5	4·0	0·7	0·5
,, old,	2·1	..	..	2·8	..	..	3·0	0·5	0·5	3·0	0·5	0·5
Days.	**5**			**7**			**10**			**17**		
	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.
Iron tannate,	1·8	0·9	0·3	1·6	0·9	0·3	1·6	0·9	0·3	1·4	1·0	0·3
Blue-black ink,	3·2	0·7	0·3	3·2	0·6	0·3	3·2	0·6	0·3	3·2	0·6	0·3
,, old,	3·0	0·5	0·5	3·0	0·6	0·5	3·0	0·7	0·4	2·85	0·7	0·3
Days.	**23**			**28**			**35**			**43**		
	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.	B.	R.	Y.
Iron tannate,	1·2	0·9	0·3	1·2	0·9	0·3	1·1	0·9	0·4	1·1	0·9	0·4
Blue-black ink,	3·0	0·6	0·2	3·0	0·6	0·2	3·0	0·6	0·2	3·0	0·6	0·2
,, old,	2·85	0·7	0·3	2·85	0·7	0·3	2·85	0·7	0·3	2·85	0·7	0·3

These are made in tints rising in measured gradations from the very faintest yellow, red, or blue to deep shades of the same colours. By using several of these glasses in combination it is possible to match any shade and to keep a record of it, so that a numerical expression can be given of the colour of the writing at the moment of examination.

For example, the writer has recorded the following changes in the colour of inks on paper in terms of blue, red and yellow on Lovibond's scale.*

* *Analyst*, 1920, xlv., 247.

When once the black pigment has attained its full intensity no further conclusions can be drawn from a comparison of the colour, until such time as the blue pigment has begun to fade away under the influence of air or light.

The black iron tannate is much more stable to atmospheric influences than the dye-stuffs used as provisional pigments, whereas the latter usually offer greater resistance to chemical agents. Hence an ink that was eventually bright blue will first become violet-black, and eventually after the lapse of possibly many years, will change to brownish-black or brown, when the blue pigment has entirely disappeared. Further details of the colour changes of inks on paper will be found in the writer's *Documents and their Scientific Examination*, p. 62 *et. seq*.

CHEMICAL TESTS OF AGE.—The formation of the iron tannate in the darkening of ink tends not only to mask the colour of the provisional blue pigment, but also to enclose its particles in such a way that they offer much greater resistance to the action of a chemical reagent. This depends upon the gradual change of a soluble iron tannate into a colloidal and finally an insoluble form.*

For example, if writing a month or two old be treated with a five per cent. solution of oxalic acid the black pigment will be bleached at once, while the blue pigment will run over the paper. After the course of three or four years the iron tannate will have become so firmly fixed upon the paper that it will only react relatively slowly with an acid reagent, and the blue pigment will show little signs of diffusion; and after another year or so the reaction will be extremely slow, and all indications of diffusion will stop. These differences are illustrated in Fig. 42, the lines of which were written with the same make of ink at an interval of ten years.

In the case of *Rex* v. *Pilcher* the writer found that the ink upon a will alleged to be twelve years old reacted immediately with several reagents and gave a copious smudging of the blue pigment, while all indications of the black pigment at once disappeared. Parallel tests applied to the inks upon a series of cheques written by the testatrix showed fairly rapid reaction and diffusion in the case of those written two and three years previously; much less rapid reaction and very little diffusion in those written five years; while after six years the reaction became very slow and there were hardly any signs of diffusion of the blue pigment. On the cheques twelve years old the ink was unaffected for a long period by the

* *cf.* Mitchell, *Fifth Colloid Report*, 1923.

reagent. The inks were proved by a series of tests to be the same kind of blue-black ink, and of a similar type to that upon the will.

In drawing conclusions from such tests care must be taken that the amount of ink, as shown by the microscope, is about the same as that upon the document in question. That is to say, heavy writing must be compared with heavy writing, and the ink must naturally be of the same type.

In abnormal cases, where an excessive amount of ink had been used, some diffusion of the blue pigment may occur even after the lapse of twelve years. But even then, it occurs only upon the surface of the writing, and does not affect the whole of the ink—whereas in recently written ink, diffusion is general and affects all the pigment present.

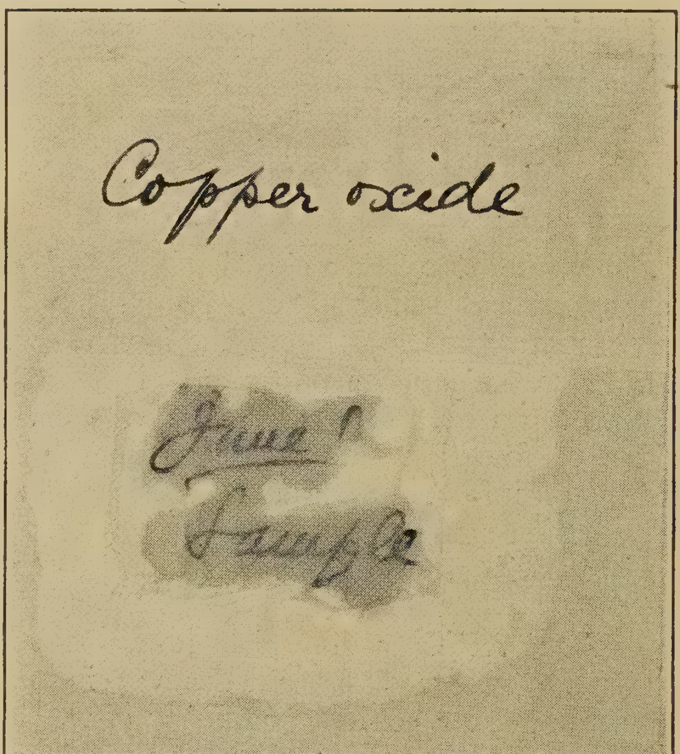


FIG. 42.—Writing of different ages treated with the same reagent.

Moreover, the microscopical appearance of the treated ink is very different in the two cases. In the old writing the letters will generally show an outline of black pigment, which has offered greater resistance to the reagent than the rest of the letters.

The copying methods suggested by *Sittl*,* *Habermann* and

* *Chem. Zeit.*, 1891, xv., 1833.

*Oesterreicher** and by *Carré*† depend upon the same phenomena of a change from a soluble to an insoluble iron tannate. The writer has shown (*Documents*, p. 70) that results obtained by such methods should only be accepted with great caution. If, however, there is pronounced difference between the copying capacity of two parts of the same document, while chemical tests indicate that the inks are of the same type, and the writing is of equal intensity, it is extremely probable that the two parts are not written at the same time.

CHEMICAL CHANGES IN THE DRYING OF INK.—When solutions of ferrous sulphate and gallotannin are mixed a pale ferrous tannate appears to be formed. This is indicated by the fact that any ferric salt present is immediately reduced to the ferrous condition, as is readily demonstrated by mixing an ethereal solution of ferric chloride and of gallotannin, when an insoluble tannate is precipitate and the ether becomes bright green. But the gallotannin is not oxidised to gallic acid, at all events, in an aqueous solution, for it can still be absorbed by hide powder. When the tannate solution is exposed to the air it is slowly oxidised and insoluble incrustations are formed, as already described on p. 111. The following table gives similar results more recently obtained,‡ and shows the effect of varying the conditions of precipitation :—

Iron Salts.		Gallotannin, etc.	Iron in Precipitate, etc. (per cent.).			
			1	2	3	4
	Grms.	Grms.				
Ferrous sulphate,	3	1	5·38	7·74	7·72	..
”	3	1 + pine oil	8·15	..	..	..
”	3	1 + H_2O_2 (small amount)	14·18	..	..	..
”	3	2 + H_2O_2 (excess)	24·29	21·05	22·4	21·46
Ferric sulphate,	2	2	6·16	17·1	..	..
”	4	3	15·70	7·7	..	..
Ferric chloride,	2	2	8·56	..	..	..

It will be seen that the earliest precipitates contain iron approximating in amount to Wittstein's iron tannate (p. 86) containing

* *Zeitsch. anal. Chem.*, 1901, xl., 725.
† *Comptes Rend.*, lxxviii., 1213.
‡ *Analyst*, 1920, xlv., p. 247.

5·53 per cent. of iron. As the oxidation proceeds the successive precipitates contain more iron, and eventually approximate in composition to the precipitate which Pelouze (p. 85) obtained by exposing a solution of ferric sulphate and gallotannin to the air.

This compound does not appear to be formed at first from ferric sulphate, but the presence of ferric salts promotes the oxidation to the more highly oxidised compound.

Hydrogen peroxide, when added in small proportion, accelerates the oxidation, and a precipitate containing 14·18 per cent. of iron, approximating in composition to Wittstein's tannate with 14·21 per cent. of iron (p. 86), is obtained. If, however, larger quantities of hydrogen peroxide are added, compounds containing from about 21 to 24 per cent. of iron are precipitated.

The addition of a few drops of pine oil to the solution of ferrous sulphate appears to have a catalytic effect. A precipitate containing 8·1 per cent. of iron was immediately obtained, so that apparently under these conditions Pelouze's tannate is formed at once. In like manner 5 c.c. of saliva accelerated the oxidation, and after two days a heavy precipitate containing 7·98 per cent. of iron was formed. The oxidation to the more insoluble form of tannate was thus accelerated, and it would seem probable that the precipitates containing amounts of iron between 5·53 and 8·1 per cent. are mixtures of these two tannates. The presence of certain substances in different kinds of galls appears to have a similar influence on the oxidation.

These two tannates when dried at 100° C., differ in their properties. The first feels like soft chalk, is somewhat soluble in water, and readily soluble in dilute hydrochloric acid. The other is more granular and has a resinous appearance, and is very difficult to dissolve completely, even in strong boiling hydrochloric acid. The intermediate precipitates show decreasing solubility as the oxidation proceeds.

These results of these experiments afford the probable explanation of the behaviour of inks in drying on paper. The tannate first formed is sufficiently soluble to allow copies to be taken for a short time, and is readily soluble in dilute acids, but as the oxidation proceeds the resinous tannate is slowly formed until eventually the tannate ink becomes not only difficult to dissolve in dilute acids, but also protects the soluble aniline dye-stuff from the action of the acid. When the oxidation has reached this stage the addition of acid will slowly cause the ink to turn blue, if the blue dye has not yet faded, but there will be little, if any, sign of diffusion or smudging (*cf.* also p. 88).

PHOTOGRAPHIC METHODS.—For several years past considerable attention has been directed to the application of the camera to the detection of alterations in manuscripts and printed matter. The chief advantages of photographic methods over chemical tests, if equally efficient, are that the document under examination is not affected in any way, and that details can be magnified to any required extent for closer examination. The latter consideration is of special importance in cases where a document forms the subject of inquiry before a court of law, and where it is necessary to demonstrate its characteristics to a judge and jury.

Mechanical Erasure.—We have previously noted that any obliteration of writing by mechanical means can almost invariably be detected by the eye, owing to the greater transparency of that portion of the paper. Such thinning of the paper would be detected still more surely by photographing it by transmitted light, the local injury appearing on the negative as a blot of greater density. If photographed in direct light the abrasion would probably not be apparent. If, on the other hand, the light were allowed to fall obliquely upon it, the roughened fibres would stand out distinctly, unless some special means had been adopted for concealing the injury (*vide supra*).

Chemical Removal of Writing.—The slight yellow stain which is usually the effect of removing writing by the application of chemical reagents, though hardly noticeable to the naked eye, will be accentuated in the photographic negative.

Destruction of Sizing.—When writing has been removed by mechanical or chemical means, the size or other dressing on the paper may be simultaneously removed. This again would often be invisible to the eye, but would be readily revealed by the camera, for any ink marks on the rough places would spread to a certain extent over the now unshielded fibres of the paper. An enlargement of a few diameters only would render manifest the rough edges of the lines.

Alterations and Additions to Writing.—It is not difficult for a skilful forger to alter letters or figures so as to deceive the casual observer. Thus a 0 might be turned into a 6 or 9, or the word "eight" changed to "eighty." These alterations would be detected by a photographic enlargement.

The writer is indebted to Mr. *A. Osborn* for the actual examples of such alterations, shown in the accompanying illustrations. Fig. 43 represents part of a cheque on which the number "11" had been converted into "17." This would probably escape notice

in the actual writing (shown in the inset), but is manifest in the enlargement.

It is often of importance to learn whether particular lines were added subsequently to the rest. For example, if the crossing of a "t" were shown to be beneath the vertical line, attention would at

FIG. 43.—Addition to figure indicated by faulty connections.

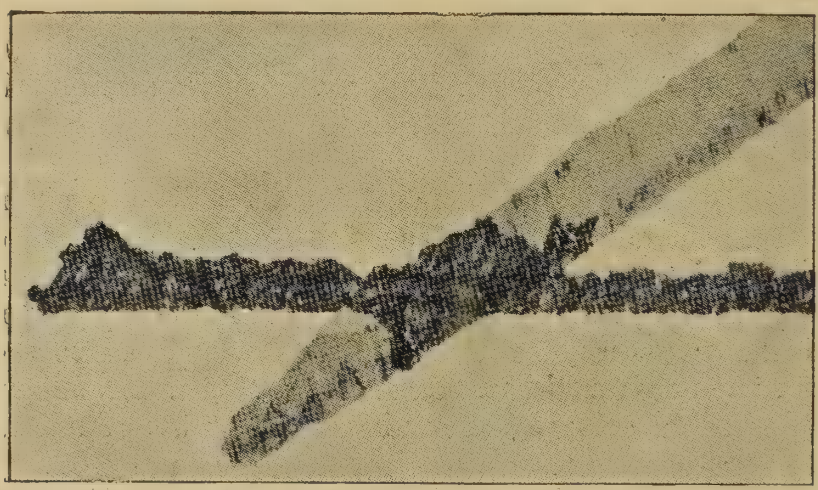


FIG. 44.—Priority of writing shown by sequence of strokes.

once be directed to the abnormal character of the writing. The way in which such sequence of lines may be shown by photography is illustrated in Fig. 44. In the case of *Rex* v. *Cohen* there was a dispute as to the date of certain entries in a doctor's day book. Since, however, one of the alleged recent entries touched the entry immediately below it at two points, and in each case the line came

below and not above the intersecting line of the subsequent entry, there could be no doubt that the suspected entry had been made prior to, and not after, those which immediately succeeded it (Fig. 45). This evidence was accepted by the Court, and the sentence on the defendant was accordingly quashed.*

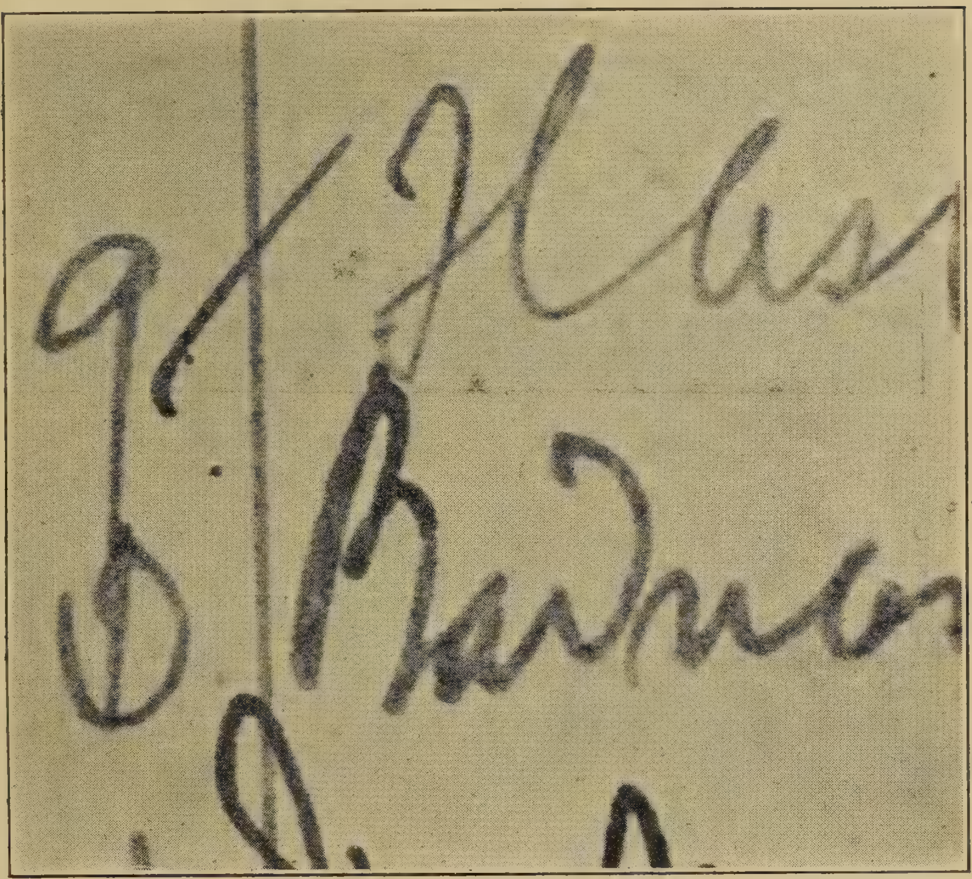


FIG. 45.—Rex *v.* Cohen. Entries in ledger showing sequence of strokes.

Fig. 46 is particularly interesting. It represents a photograph by transmitted light, showing that the original figures punched in a cheque for $24 had been carefully filled in, and $2400 had been punched on the same ground.

For further particulars of the application of scientific methods to the examination of handwriting, the reader may be referred to *Osborn's* standard work.†

Photographic Distinction between Different Inks.—Jeserich ‡ was

* See *Analyst*, 1920, xlv., 247 ; *Documents*, pp. 65-69.
† *Questioned Documents*, Rochester, N.Y., 1910.
‡ *Journ. Roy. Phot. Soc.*

the first to assert that inks apparently black were really brown, blue, or red in tint, when dry upon the paper; and that such differences were clearly shown in an ordinary photographic negative, and still more so in one taken by the isochromatic method. This statement has been repeated by *Minovici*,* and quoted in different journals.

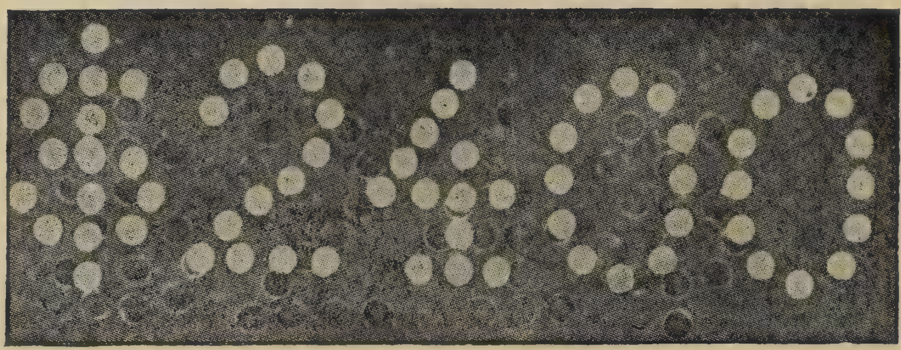


FIG. 46.—Substitution of new for old perforations.

We have made experiments as to this point, writing a series of words with different commercial inks. In the case of blue-black inks, differences of intensity were distinctly visible to the eye, and the photograph taken on an ordinary plate by daylight revealed no more.

We have also photographed the same writing with a Cadett spectrum plate and "Absolutus" screen, without attaining any different effect. It is evident that this method, even if it yield good results in particular cases, such as distinguishing between a chrome-logwood and a blue-black iron-gall ink, is not generally applicable.

* *Bull. della Soc. Fotograf. Italiana*, 1900, xii., 349.

SECTION II.

PRINTING INKS.

CHAPTER VIII.

EARLY METHODS OF MANUFACTURE.

CONTENTS.—Historical—China—Greece and Rome—England—Early printed books—Early methods of manufacture—Fertel's method of making ink—Breton's method—Savage's method of manufacture—Modern methods of preparing ink.

I.

HISTORICAL.—*China.*—A work which is said to have been written during the reign of *Wu Wang*, about 1200 B.C., makes mention of the blackening of engraved characters, but it does not seem to be clear whether this refers to inscriptions on stone which would be thus rendered more legible—a method still in use by monumental masons—or to blocks to be afterwards used to yield impressions upon another surface. It seems certain, however, that a primitive mode of printing was known to the Chinese as early as 50 B.C., but that not much advance was made until the reign of *Ming-Tsung*, 927 A.D., when certain volumes were printed from stone blocks for the Imperial College at Pekin. In this early example of the printer's art the characters were cut into the surface of the stone, so that when printed they would appear as white on a black ground. Shortly afterwards engraved blocks of wood, with the letters in relief, were used for another edition of the same work. In the eleventh century an ingenious Chinese block was made, with cut or moulded characters in cubes of porcelain, and these, after being baked to harden them, were pressed into a block of cement so that they could be printed from. The method was not followed up.

The adoption of movable types in China was rendered difficult for the reason that in the Chinese language the words cannot be resolved into the letters of an alphabet. Each word requires a separate character, and as there are about 80,000 of them, of which,

however, only 14,000 to 15,000 are in common use, the Chinese printer must be a man of exceptional agility. Nevertheless, a large number of books and periodicals are now printed in China. It is obvious that the Chinese had only to add varnish to the black pigment familar to them in order to compound a good printing ink.

Greece and Rome.—Although both the Greeks and Romans were acquainted with the art of engraving on metals at a very early period, there is no trace of any attempt being made to transfer designs so cut to other substances, if we except certain stamps which were employed to mark bricks and articles of pottery. There was no inducement to stimulating invention in this direction while slave labour could be employed for writing documents, and we can easily imagine that with the decline of Roman culture literature would only be cultivated by the very few. But as soon as paper began to be known, and was recognised as a unique material for letter-writing and for the making of books, the minds of many must have instinctively turned to the possibility of multiplying copies by an engraved surface, and an impression-giving medium.

England.—*Caxton* came to England and set up a press in Westminster about A.D., 1477 (the exact date has not been ascertainable), but the first paper mill was not established in England until 1498. The printing press was therefore ready nearly twenty years before the means existed in this country of supplying it with its first requisite. But in Italy and Germany paper mills were at work in the thirteenth century, and in France, Switzerland, and Austria in the fourteenth. The arts of printing and paper-making naturally reacted one upon the other for the advantage of each, and the Chinese are believed to be the first nation which benefited by their partnership.

EARLY PRINTED BOOKS.—Many examples of early printing can be seen in the galleries of the British Museum ; and it is interesting to examine the specimens displayed in cases in the King's Library there, if only to note the manner in which they have, with very few exceptions, preserved their pristine appearance.

Block Books.—Beginning with the block books, *i.e.*, books in which both cuts and letterpress were cut in solid wood blocks, we find that the earliest bears the date 1470, and we learn from the catalogue that "the long accepted belief that letter-printing from the solid block was necessarily prior to that from movable types, and must, therefore, have been introduced by about 1440, is now seriously challenged."

The block book was only used for works of a popular character, and answered the purpose of the modern stereotype block from

which a number of copies can be printed without the necessity of resetting type. These early books were presumably printed without the help of a press, the impression being obtained by rubbing the back of the sheet while it was in contact with the thinly inked block. Only one side of the paper was printed, the other being left blank. In later examples, however, both sides of the paper were printed on, and it is interesting to note that the ink penetrated sufficiently into the substance of the paper to be distinctly seen through as the page lies open in its present situation.

In Case I., which is devoted to these block books, the first example exhibited, the product of an unknown printer in the Netherlands, shows that an ink has been employed which was either brown in colour originally, or has faded to that hue. The more probable explanation is that the ink was made of an impure carbon, which would give a brown tint. In all the other examples in the same case the printing ink is of a full black, although instances are not wanting in which for lack of liberality on the part of the printer it does not present a complete opacity.

These early works follow the old manuscript model in the possession of large ornamental initials, and other adornments which were afterwards added by the "rubricator." In one specimen we can note that the capital letter at the commencement of every sentence has an upright stroke of red, which has as obviously been executed by hand as has been the rough colouring of some of the picture blocks. The specimen referred to is known as the 42-line Bible, which is attributed to the press of Gutenberg at Mainz, about 1455. The red colour has apparently much deteriorated, and it would be interesting to know the nature of the pigment. In another example, the 36-line Bible, also from Mainz, the red initials show a full scarlet.

German Books.—In Case V., which is devoted to examples of early printing from Germany, we find the first illustrated edition of Virgil, 1502 A.D., with a preface in which the compiler boasts in Latin verse that by the help of the pictures the ignorant will be able to follow the text as well as the learned. The illustrations are certainly very good, with engraved lines of such fineness that they must have required an ink of fair quality to do them justice. There is no trace of fading in any of these books, nor should we expect to find any. For carbon is imperishable except by the agency of fire, and, happily, as it is the most easily obtained and cheapest black pigment known, it was naturally adopted by the first printers.

In some cases the ink is seen to have "set off" on the opposite page, a fault from which modern books are by no means free,

showing that the varnish used with the carbon was improperly prepared, or that an impure form of lamp-black was used.

Italian Books.—In Case VI., Italy, 1465-1472 A.D., we find specimens of printing which are very brown in tone. In one example, especially No. 7, there are two full-page drawings (wood blocks), which appear as if printed in strong vandyke brown. The engravings on the hidden sides of the leaves are seen through the paper so distinctly as to give the idea that the ink must have contained some large excess of oil, so that it penetrated through the fibres of the paper.

Dutch Books.—In Case IX., Netherlands, there is a specimen with brown ink which compares unfavourably with the brilliant black of the ink in other exhibits in close proximity to it. Another specimen shows the paper yellow and soiled, while the print is strong. In this example there are some marginal notes in a very much faded writing ink. It is quite possible that the brown tint observable in some of these old specimens of the printer's art is due to the use of carbon prepared from the soot of burning wood, or peat. Such a product has long been in use as a brown pigment by water-colour painters under the name of bistre.

Early Methods of Manufacture.

The old wall ink (*atramentum tectorium*) described by *Pliny* is the forerunner of our printing ink, which is essentially a kind of rapidly drying black paint.

One of the earliest printed accounts we possess of the manufacture of printing ink is that given by the Venetian *Canneparius* * in his book on inks published in 1660. His ink consisted of 1 lb. of a varnish of linseed oil and juniper gum thoroughly incorporated with 1 oz. of smoke-black, and boiled over a slow fire to the required degree of consistence.

According to the description given by *Moxon* in his *Mechanick Exercises* † in 1683, the printing ink then made in England was very

* *De Atramentis*, p. 260.

† *Moxon's* actual words are worth quoting, if only on account of their quaintness :—" The providing of a good inck, or rather good varnish for inck, is none of the least incumbent cares upon our master-printer, though custom has almost made it so here in England ; for the process of making inck being as both laborious to the body, as noysom and ungrateful to the sence, and by several odd accidents dangerous of firing the place it is made in, our English master-printers do generally discharge themselves of that trouble ; and instead of having good inck, content themselves that they pay an inck maker for good inck, which may yet be better or worse according to the conscience of the inck maker."

inferior to the Dutch ink. The main differences were that in the latter only linseed oil and little rosin were used, that the oil was better prepared, and that the varnish was only incorporated with the black by the pressmen immediately before use ; whereas in the manufacture of the English ink much rosin (and frequently fish oil) was added to the linseed oil, which was also insufficiently boiled, so that the ink was oily and separated in the paper.

Manufacture of Dutch Printing Ink Varnish.—A cauldron was half filled with linseed oil, covered, and heated over a brisk fire until the oil boiled. When heated to a sufficient temperature the oil was fired several times, being each time extinguished by means of the cover until eventually a varnish of the required consistence was obtained, this point being determined by cooling a few drops on an oyster shell and testing it between the finger and thumb. It was then allowed to cool somewhat, and clarified by squeezing it in the hand through linen.

When rosin was added, it was used in the proportion of ½ to 1 lb. to each gallon of oil. *Moxon* asserted that the addition of too much rosin made the ink become yellow : but *Savage* denied this, since in his experience rosin thickened the oil, and prevented its separating from the ink and spreading through the paper.*

Moxon stated that suitable varnish might be made without actually *burning* the oil ; but here again *Savage's* experience was that, although when linseed oil was boiled until viscous it yielded a clean and workable ink, yet after a few days the oil separated to some extent and spread through the paper.

Savage considered that, whilst *Moxon's* strictures on the English press work of the seventeenth century were justifiable, yet compared with the English ink of the early nineteenth century this boasted Dutch ink would have been regarded as worthless.

FERTEL'S METHOD OF PREPARING INK.—*Fertel*, a French printer of St. Omer, published a work on pressmanship in 1723, in which he described the manufacture of printing ink.†

This was prepared by heating linseed or nut oil in a pot with an adjustable cover until the vapours became inflammable (about 2½ hours), a crust of bread being introduced to " withdraw grease from the oil," and removed when carbonised. The oil was then withdrawn from the fire, the pot uncovered, and the vapours allowed to burn. The addition of turpentine oil, advocated by some printers, was objected to by *Fertel* on the ground of its making the ink clog the face of the type.

* *The Preparation of Printing Ink*, 1823, p. 29.

† *La Science pratique de l'Imprimerie.* St. Omer. 1723.

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The varnish thus prepared was incorporated with smoke-black from pitch resin collected in a chamber hung with sheep-skins, the usual proportions being 5 ozs. to 2 lbs. of varnish, and the ink was ground thoroughly and worked upon the inking-table. In *Savage's* opinion this proportion of lamp-black was too small for a good ink.

BRETON'S METHOD.—In 1751 *Breton*,* printer to the King of France, published an account of a very similar method of preparing printing ink. For the manufacture of 100 lbs. of varnish, 110 to 112 lbs. of nut oil were heated in a closed copper or iron vessel, which was usually pear shaped, on a clear fire for about two hours. It was then removed and "burnt," the process being repeated several times. Finally, it was boiled over a slower fire for three hours until of the consistence of glue, when it was strained through linen. Turpentine oil and litharge were not recommended by *Breton* on the ground of their clogging the type.

This "burnt oil" or varnish was thoroughly incorporated by the pressmen, on the inking-table, with lamp-black in the proportion of 2½ ozs. to 1 lb.

Breton's recipe has become a standard one, and was copied into the books of different later writers, such as *Lewis* (1763), *Papillon*, etc.

The method of boiling was substantially identical with the Dutch method described by *Moxon*. *Savage* endorses *Breton's* condemnation of the use of litharge in the preparation of the varnish.

The sixth edition of the *Encyclopædia Britannica* (1823) was apparently the first to publish any substantial difference from these early methods in the manufacture of printing ink, the improvement being the addition of soap to the constituents, an addition which, though probably well known to certain manufacturers, had been kept as a trade secret. The effect of the soap was to cause the ink to leave a clean and sharp impression on the paper, to prevent the type from becoming clogged, and to prevent the ink from "skinning" when kept.

In the *Encyclopædia* recipe the burnt oil was mixed while still warm with 2 lbs. of black rosin and 1 lb. of hard soap in slices. In *Savage's* opinion this amount of soap is too much, and would be liable to make the ink daub the type and produce blurred impressions.

SAVAGE'S METHOD OF MANUFACTURE.—In 1823 *Savage*, who had studied the manufacture of printing ink from the point of view of the practical printer, published a book on the subject, in which he discussed all the previous methods of manufacture.

For the preparation of the varnish he recommended the use of

* *Encyclopédie Methodique*, vol. v., p. 633.

old linseed oil and black or amber rosin, which was melted into the oil at a temperature of not less than 306° F., the approximate melting-point of the rosin.

Six quarts of linseed oil were heated in a pot over a brisk fire, and the vapours tested with a light from time to time. When the flashes produced became stronger, the pot was removed, and the oil fired while kept continually stirred with an iron ladle. The flame was extinguished occasionally by placing the cover over the pot, so as to test the consistence. When, on cooling, it could be drawn into strings about half an inch in length, it was judged to be sufficiently burnt for book-work.

Care was taken to prevent the oil frothing up through too violent heating, and thus running the risk of the entire mass bursting into uncontrollable flame.

After cooling somewhat in the covered vessel, the "burnt" oil was mixed with six lbs. of rosin, gradually stirred in, and then with $1\frac{3}{4}$ lbs. of brown soap in thin slices, and was finally heated to the boiling-point.

This varnish, while still warm, was next poured, little by little, into an earthenware vessel containing 5 ozs. of Prussian blue or indigo, or a mixture of these, 4 lbs. of mineral lamp-black, and $3\frac{1}{2}$ lbs. of vegetable black, and the whole was stirred until free from lumps, and finally ground in a levigating mill.

MODERN METHODS OF PREPARING PRINTERS' INK.—Although the old method of preparing printer's or lithographic varnish, by heating the linseed oil until inflammable vapours are given off, and setting fire to these, is still in use, it has been found that the actual burning of the oil is not an indispensable part of the process, and various other methods of thickening the oil and converting it into varnish are now employed.

Other ingredients are also added to the linseed oil varnish, in addition to the rosin and soap used in *Savage's* time, and this is especially the case with the cheaper kinds of inks such as are used for newspaper work. Various processes for preparing a black pigment to be used in place of lamp-black have also been described in patents taken out during the last thirty years.

CHAPTER IX.

MANUFACTURE OF VARNISH.

CONTENTS.—Boiled oils—Burnt oil—Varieties of lithographic varnish—André's apparatus for boiling oil—Apparatus with steam jacket and air blast—Boiling with superheated steam—Treatment with oxygen—Linseed-oil substitutes—Addition of driers—Gloss inks.

BOILED OILS.—The oils classified under the term "drying oils" are distinguished from other oils by the greater rapidity with which they form a solid varnish on exposure to the air at the ordinary temperature. Strictly speaking, this difference is one of degree rather than of kind, for it has been shown that even oils, such as olive and almond oils, do eventually dry after the lapse of a long time. The principal drying oils are linseed, walnut, hempseed, poppyseed, nigerseed, and the curious tung, or Chinese wood oil. For the characteristics and methods of examining these oils the reader is referred to works on the analysis of oils. Other oils, such as cotton-seed, maize, soya bean and menhaden oils, occupy an intermediate position between the "drying" and "non-drying" oils, and are usually known as "semi-drying" oils. The drying capacity of oils is usually attributed to the presence of a considerable amount of the liquid fatty acids, linolenic and isolinolenic acids, whilst another acid, linolic acid, probably contributes to the process.

Fixed vegetable and animal oils consists in the main of compounds of glycerin with saturated and unsaturated fatty acids, the latter predominating. Thus, olive oil consists principally of a compound of glycerin and oleic acid, $C_{18}H_{34}O_2$; cotton-seed oil contains a large proportion of glycerides containing linolic acid, $C_{18}H_{32}O_2$; whilst linseed oil and other "drying" oils are characterised by the amount of the still more unsaturated linolenic and isolinolenic acids, $C_{18}H_{30}O_2$, they contain.

Each of these unsaturated fatty acids and their glycerin compounds (glycerides) are capable of entering into combination with chlorine, bromine, or iodine, forming saturated compounds. Oleic acid, for instance, yields oleic dibromide, $C_{18}H_{34}Br_2O_2$; linolic acid gives linolic tetrabromide, $C_{18}H_{32}Br_4O_2$; and linolenic acid, linolenic hexabromide, $C_{18}H_{30}Br_6O_2$.

In like manner, they are capable of being saturated with oxygen, and this is part of the change that occurs when a film of drying oil hardens into a varnish on exposure to the air, whilst the process can be considerably accelerated by subjecting the oil to a preliminary treatment known as "boiling."

In this process, the exact nature of which still needs elucidation, considerable alteration of the "raw" oil takes place during the partial oxidation. Such boiled oils were at one time prepared solely by means of heat, but subsequently various substances, known as "driers," were added to accelerate the oxidation, which was also promoted by injecting hot air into the hot liquid.

Of the various "driers," which appear to act mainly as conveyors of oxygen from the air to the oil, salts of lead and manganese and more recently cerium, in the proportion of a few pounds to the ton, have been found the most satisfactory, and are the most frequently used.

The varnish used in the manufacture of printer's ink differs from the varnish used by painters and lineolum manufacturers in being prepared without the addition of any "driers" whatever. It is also as a rule much paler in colour.

The apparatus used in the old method of boiling oil consists of a kettle, which is heated over a free fire (Fig. 47). Over this is suspended a lid, which can be lowered to close the vessel and immediately extinguish the flames when the evolved vapours take fire. To prevent frothing, the pan is only filled to half its capacity with oil.

BURNT OIL.—In preparing oil for the manufacture of printing ink, the process of oxidation is carried still further than in the process of boiling. In the old process of firing, as described in the preceding pages, the oil becomes very dark in colour, and apparently undergoes considerable decomposition, probably attended with polymerisation similar to that which occurs in the vulcanisation of oils by means of sulphur chloride.

The amount of free acid liberated in the oil during the process is much greater than in the case of oil that has been boiled for a very long time at a temperature of 260° to 300° C.

Printers' varnish thus prepared has good drying properties, and is considerably denser than the raw oil (*vide infra*).

Leeds * gives the following details of the method of boiling oil for lithographic varnish:—The kettle is filled to about two-thirds of its capacity with linseed oil that has been kept in store for some time. As soon as the water has been expelled and the froth of albuminous impurities skimmed off, the temperature is raised to about 500° to 560° F., and the boiling continued until the required

* *Journ. Soc. Chem. Ind.*, 1894, xiii., 203.

degree of consistency is attained, after which the varnish is left to cool and settle and is decanted into storage tanks.

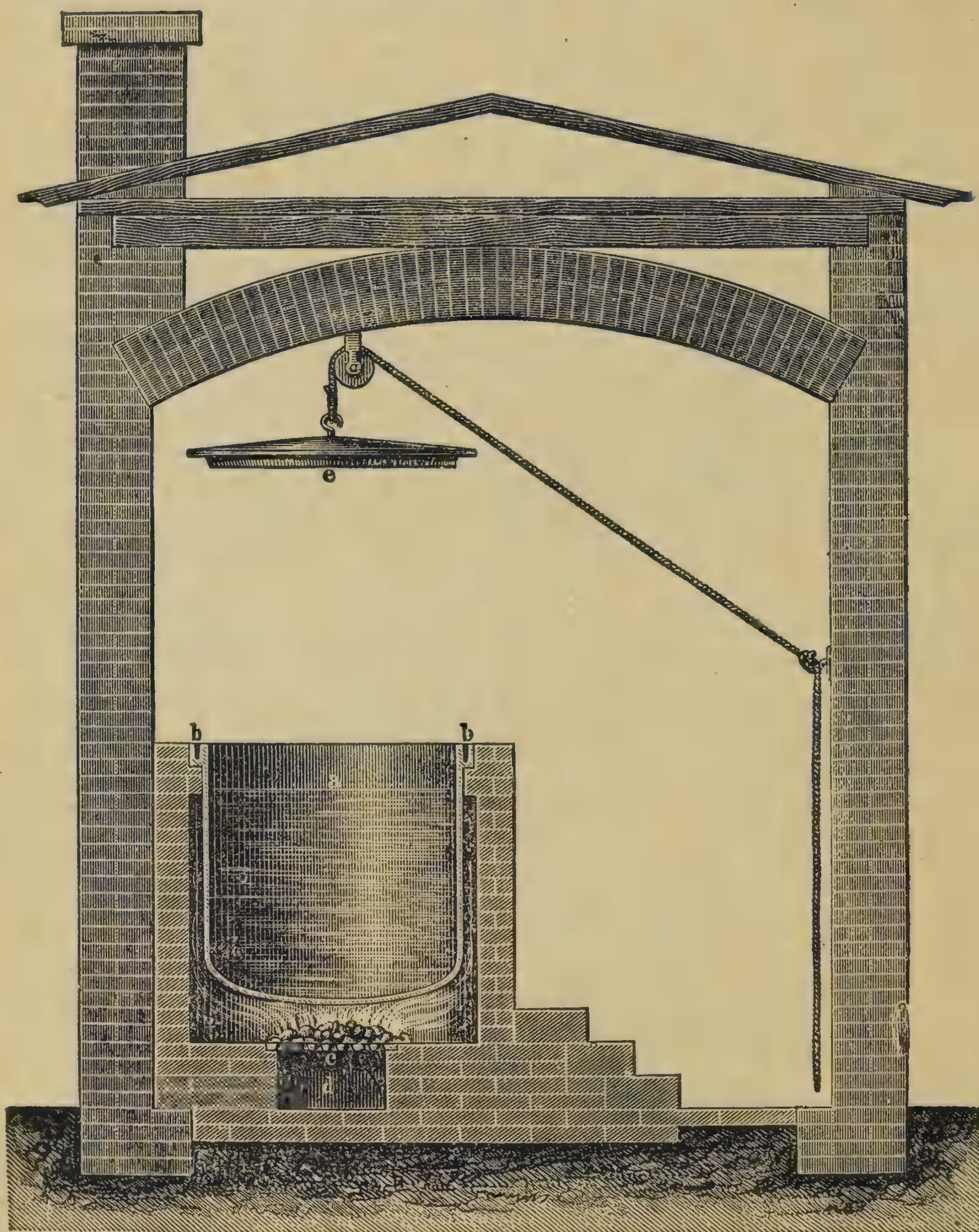

FIG. 47.—Free-fired pan for boiling oil.

The time required depends upon the temperature of boiling and on the maturity of the raw linseed oil. A high temperature accelerates the conversion but has the drawback of producing a darker product.

Leeds lays considerable stress on the importance of using a well

matured oil. Crude linseed oil immediately after expression contains impurities which separate out to a greater or less extent on standing for a few months. If such crude oil be used for boiling there is much more froth and a poorer yield of a darker varnish, whilst the time and consumption of fuel are greater.

The ordinary loss ranges from about 3 to 10 per cent., according to the maturity of the oil.

It is interesting to note that the importance of using an old oil in the preparation of the varnish was recognised by all the older writers from *Moxon* to *Savage*.

VARIETIES OF LITHOGRAPHIC VARNISH.—Five or six varieties of lithographic varnish are in use, ranging in consistence from a very thin product to one of extreme viscosity. These are termed "extra strong," "strong," "middle," "thin," "tint," and "thin tint," according to their degree of viscosity. *Leeds* (*loc. cit.*), who had thoroughly studied the chemical changes that took place in the conversion of the raw oil through the various intermediate changes into "extra strong" varnish, pointed out that the most viscous products have less drying capacity than the thinner varnishes, and that their viscosity, which gave them greater carrying power as a medium for pigments, was their chief recommendation.

The following table, abridged from that of *Leeds*, represents some of the changes undergone by raw linseed oil in this process of boiling, and in the old method of igniting the vapours to produce "burnt" oil:—

Varnish.	Specific gravity at 15.5° C.	Free acids as oleic acid.	Saponification value.	Iodine value.	Unsaponifiable matter
		Per cent.			Per cent.
"Tint" . .	0.9584	1.46	197.5	113.2	—
"Thin" . .	0.9661	1.76	196.9	100.0	0.62
"Middle" . .	0.9721	1.71	197.5	91.6	0.85
"Strong" . .	0.9741	2.16	190.9	86.7	0.79
"Extra strong" .	0.9780	2.51	188.9	83.5	0.91
"Burnt" thin .	0.9675	6.93	195.5	92.7	1.35

ANDRÉS' APPARATUS FOR BOILING OIL.—This apparatus (Fig. 48) consists of a cylindrical copper kettle, *A*, to the middle of which is attached the collar *D*, which supports it in the furnace. The top of the vessel is bound by a strong iron ring, to which are attached the chain and tackle *C*, thus enabling the vessel to be

rapidly withdrawn from the fire by means of a crane. The lid, *B*, fits closely to the upper ring, forming a nearly air-tight joint, so that flames can be immediately extinguished. Above the furnace is fixed a hood provided with a flue to conduct away the vapours.

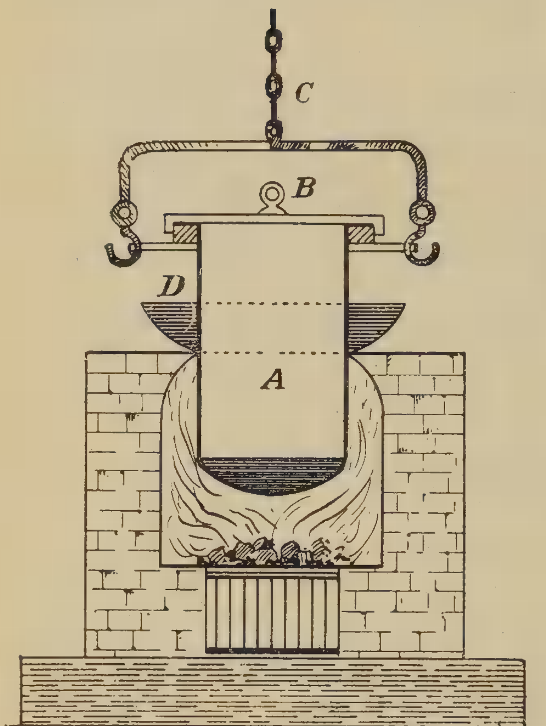

FIG. 48.—Andrés' apparatus.

It was asserted by *Savage*, and accepted for long afterwards, that actual ignition of the vapours from the oil was essential for the production of a varnish suitable for printing ink. It is now known, however, that the same result can be obtained by boiling the oil at a higher temperature than in the preparation of ordinary boiled oil for paints.

APPARATUS WITH STEAM JACKET AND AIR BLAST.—A pair of steam-heated kettles, each of which takes a charge of about 350 kilos., is shown in Fig. 49. These are constructed with jackets capable of resisting a pressure of several atmospheres. The oil is heated by steam

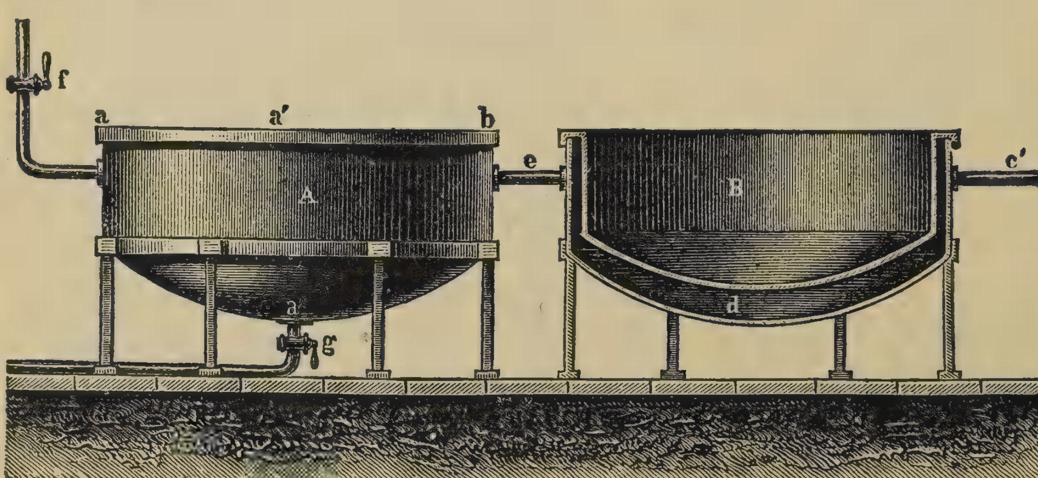

FIG. 49.—Steam-heated kettles.

at about 130° C. or higher, under a pressure of four to five atmospheres, while air is blown through until the varnish is of the required

consistence. Each kettle is covered with a dome-shaped cover, in which there is an outlet pipe for the escape of the vapour evolved. The steam enters the jacket of the pan B at c′, and passes through e into the jacket of the pan A. At f is a cock for blowing off, which is so regulated that only a little steam escapes, while the condensed water is drawn off through the tap at g.

Frederking's apparatus for boiling oil contains a steam coil, round which has been cast the metal forming the pan. Steam under a required pressure is passed through the coil, and the contents of the kettle readily raised to temperatures of 350° to 400° C. without danger, the pressure being solely on the piping and not on the metal pan itself.

An apparatus described by *Andrés* * contains a circular iron pipe supported on the bottom of the vessel, and connected with bellows by means of a vertical tube. Air is blown into the oil through small holes, about 0·5 cm. in diameter, in the circular pipe, and the heated oil is kept in motion during the thickening process. When cold air is blown into the oil the temperature is kept below 270° C. to prevent the varnish becoming too dark in colour.

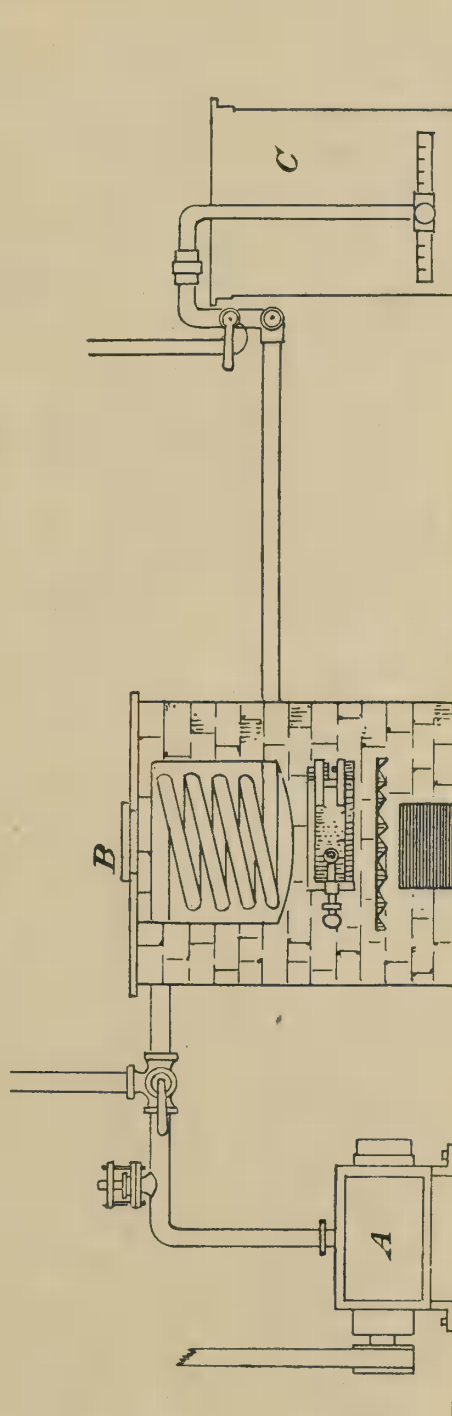

FIG. 50.—Apparatus for hot-air treatment of oils.

Sauer's Apparatus.—This consists of a heating vessel in which a paddle agitator is made to revolve round a central shaft, whilst a current of hot air enters near the bottom of the apparatus.

* *Drying Oils*, 1901, p. 237.

Fig. 50 shows another apparatus for preparing varnish by this method. The air is driven by means of the pump *A*, through the coil *B*, and is heated to the required temperature before entering the oil in the vessel *C*, through the small openings in the pipe.

The varnish produced by this method dries well, but is usually somewhat darker than that produced by the ordinary method, especially if the temperature be allowed to rise too high.

A modern steam-jacketed mixing pan, which is suitable for boiling linseed oil, is shown in Fig. 51. It is provided with a mechanical agitator driven by means of the bevel-gear wheel, and has a pipe ending in a blowing coil at the bottom of the vessel and connected with an air-pump.

BOILING WITH SUPER-HEATED STEAM.—Apparatus in common use for this purpose consists of a kettle containing a coil through which passes steam heated to a temperature of about 400° C. by being passed through a super-heater kept outside the chamber. The kettle is provided with a cover which can be easily removed by means of a chain and tackle, whilst an exit pipe in this cover conducts the escaping vapours to the bottom of the superheater, whence they are drawn up into the fire and consumed. Hence the process is accompanied by little or no smell.

Lithographic varnish thus prepared has the drawback of being darker in colour than ordinary "boiled" varnish, but, on the other hand, the process is much more rapid.

TREATMENT WITH OXYGEN.—Very pale varnishes are obtained by subjecting linseed oil, heated to a moderate temperature, to the action of oxygen. Instead of losing in weight, as in the ordinary boiling processes, the varnish shows an increase of about 4 per cent. through the addition of the oxygen.

Leeds (*loc. cit.*) found that varnishes thus prepared were free from the brownish-green fluorescence of ordinary lithographic varnishes, but that they possessed a much more unpleasant odour.

In a process protected by "Brin's Oxygen Co." (Eng. Pats., No. 12,652, 1886; and No. 18,628, 1889) a current of pure (90 to 93 per cent.) oxygen is passed into the space above the oil, instead of being blown through it. The apparatus used for the purpose consists of a closed steam-jacketed pan, in which the oil is kept in motion by a revolving agitator. The oxygen is introduced when the oil has been heated to nearly 100° C., and is absorbed, at first slowly, and eventually more rapidly than it is supplied. So much heat is produced by the reaction that it is ultimately necessary to cool the jacket by admitting water into it.

FIG. 51.—Steam-jacketed Heating Pan for Boiling Oils.

Linseed oil varnish prepared by treatment with oxygen differs from the original much more than varnish prepared by boiling. Thus it contains about ten times as much free acid, and has a considerably higher specific gravity, whilst its absorption capacity for iodine is much lower.

Leeds (*loc. cit.*) gives the following results obtained in the analysis of two samples of these oxidised linseed oils :—

Varnish.	Specific gravity at 15° C.	Free acids as oleic acid.	Saponification value.	Iodine value.	Unsaponifiable matter.
		Per cent.			Per cent.
Oxidised oil, weak .	1.03	18—28·4	221	58.8	0.87
Oxidised oil, strong .	1.05	18.5—28.9	223.5	53.5	0.97

For the methods of examining linseed oils and lithographic varnishes see *Alder Wright* and *Mitchell's Oils, Fats and Waxes.*

TREATMENT WITH OZONE.—It was shown some years ago by *Schrader* and *Dumcke* that a varnish is rapidly produced by the action of ozone upon raw linseed oil, which is also bleached in the process.

Apparatus for the purpose was subsequently patented in Germany by *Graf & Co.*, a current of ozone from any suitable generator being conducted through the heated oil. Care is needed in this operation to prevent the oxidation proceeding too far, or a semi-solid caoutchouc-like mass is obtained. In fact, patents for preparing commercial rubber substitutes by the action of the ozone under pressure upon linseed and other oils have been taken out by *Rosenblum* and *Rideal* (Eng. Pat., No. 9529, 1897 ; and No. 6464, 1898).

Ramage (Eng. Pat., No. 7242, 1901) has devised a process for making varnish of good drying capacity by heating non-drying oils with ozone in the presence of an oxygen-occluding substance, such as platinised asbestos.

Müthel and Lütke's Electric Process.—In this process, patented in Germany (Ger. Pat., No. 29,961), the oil is treated with a mixture of gases (*e.g.*, oxygen with steam, or nitrous oxide with air or oxygen) which has been subjected to the action of a powerful electric discharge whilst passing through a series of condensers. The

oil is heated by means of a steam coil, whilst the gaseous mixture enters through holes in a small spiral in the bottom of the tank. The volatile products of the reaction and the unused gas are drawn off by a pump at the top.

LINSEED OIL SUBSTITUTES.—Numerous substances have been proposed as substitutes for linseed and other drying oils. An ink containing none of the ordinary oil varnish was described by *Savage* in 1823 (*loc. cit.*), and methods of preparing other varnishes of the same kind can be found by reference to the patent list at the end of this book. One of the most interesting of these is a natural drying mineral oil, which is found in Java and known commercially as Grisel oil. The use of this is claimed by *Stoop* (Eng. Pats., No. 24,504, 1897 ; and No. 23,071, 1898).

Greenstreet (Fr. Pat., No. 446,475, 1912) has claimed a process for converting hydrocarbon oils into oils capable of evaporating without leaving a residue. They are first heated with steam at 205° to 535° C., and the mixture of oil and steam injected into a coil heated to 425° to 535° C., after which they are passed through a series of condensers. The products are stated to be suitable as "driers" for use with pigments.

ADDITION OF DRIERS.—To accelerate the speed of drying and prevent smearing *Heyl* and *Baker* (Eng. Pat., No. 10,055, 1913) add about 0·25 per cent. of sodium amyl sulphate to the ink.

Dyke-Acland (Eng. Pat., No. 5347, 1913) claims the addition of Ceara rubber seed to facilitate the drying of linseed oil.

"Driers" of some sort are commonly added to the varnish when speed of drying is an essential, as, for example, in newspaper work. For this purpose the linseed oil is boiled with about 17 per cent. of its weight of litharge and five per cent. of lead acetate for three hours and subsequently thinned with turpentine oil to the desired consistency.

Seymour * gives the following formula for a rapid drier for press work: Iron sulphate, 12 lbs.; lead acetate, 12 lbs.; and litharge, 6 lbs.

Gloss Inks.—The so-called "gloss inks," which as their name indicates are intended to have a glossy appearance when dry, contain a suitable "drier" and a quick drying resin varnish, such as copal.

In the cheapest newspaper inks rosin is a common ingredient, while oil of turpentine or its substitutes is added to others.

Methods of testing the purity of turpentine will be found fully described in the *Analyst*.

Other ingredients of cheap inks are paraffin oils, which serve to

* *Modern Printing Inks*, p. 68.

dilute the varnish. They retard the drying of the ink, but are gradually absorbed by the paper.

Soya Bean Oil.—The oil contained in the soya bean dries fairly well, although not so rapidly as linseed oil. It is now largely used, in the United States, either by itself or mixed with linseed oil, as a liquid medium for printing inks. Like linseed oil it requires to be polymerised by " boiling " before it can be used as a printing ink varnish.

Semi-drying Oils, such as menhaden oil, are also used as substitutes for the more expensive linseed oil, especially in America.

CHAPTER X.

PREPARATION AND INCORPORATION OF THE PIGMENT.

CONTENTS.—Black for printing ink—Modern apparatus—Thenius' lamp-black furnace—Furnace for producing black from pitch—Other black pigments—Carbon blacks—Purification of lamp-black—Composition of lamp-blacks—**Methods of examining lamp-blacks and gas-blacks**—**Mixing the black and varnish**—Mixing the varnish and lamp-black—Quack's mixing machine—Werner and Pfleiderer's mixing machine—Torrance's mixing machines—**Grinding**—Torrance's grinding machines—Machines by Neal, Jackson, Kingdon—Lithographic printing ink—Lithographic chalks—Collotype ink—Luminous printing ink.

BLACK FOR PRINTING INK.—The nature and degree of purity of the black pigment incorporated with the varnish is of the highest importance, especially in the case of ink intended for fine-art printing, since the depth and permanency of the tone largely depend on this. Hence many printing ink manufacturers prepare their own lamp-black, so as to have the entire manufacture under their control, and to be able to produce an absolutely uniform product. Some of the older methods and apparatus used in the preparation of lamp-black have already been described in Chap. I., and here it is only necessary to describe some of the more modern apparatus.

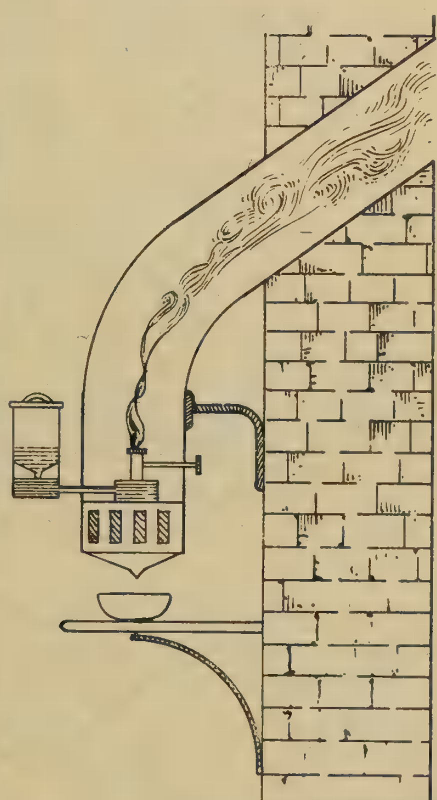

FIG. 52.—Lamp-black apparatus.

Fig. 52 represents a modern apparatus used for the production of lamp-black from oil, and is a development of the ancient method. The supply of oil is regulated by the small chamber outside, while the air enters through holes beneath the lamp. The smoke from the

lamp is conducted through the chimney into a chamber, where it is deposited and collected.

Another apparatus intended for the rapid production of a coarser lamp-black is shown in Fig. 53. It consists of a revolving cylinder, through the interior of which passes a current of cold water. A series of lamps is kept burning below this, and the smoke deposited on the cylinder is removed by means of the brush.

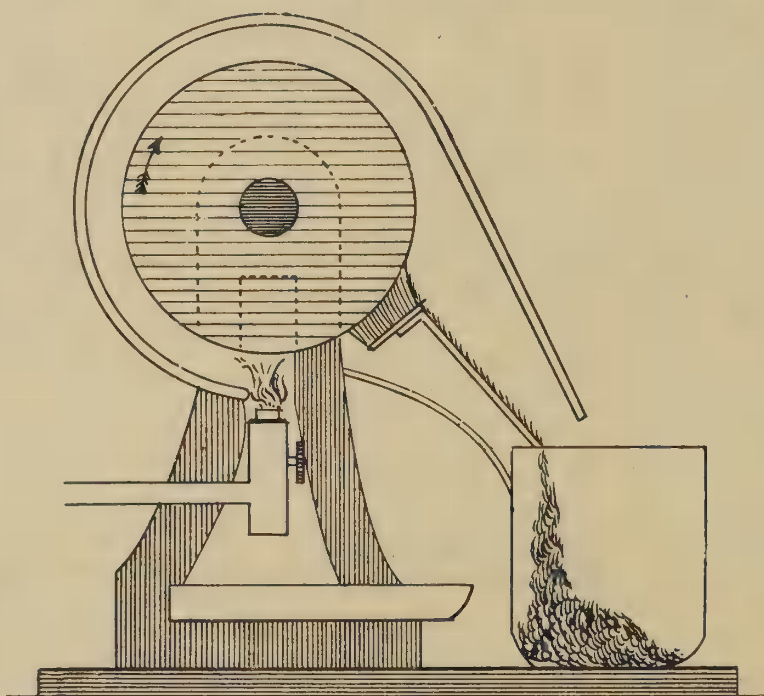

FIG. 53.—Lamp-black apparatus.

THENIUS' LAMP-BLACK FURNACE.—This apparatus, devised by *Thenius* for the collection of lamp-black from coal-tar oil, consists of a series of iron chambers opening into one another. In the first of these the oil, freed from naphthalene as far as possible, falls drop by drop from a tank above on to a red-hot plate, over which passes a limited supply of air. The smoke is carried through the series of chambers, forming black deposits of different grades of fineness on the walls. About 70 kilos. of smoke-black are obtained from 400 kilos. of the oil, about half of it being of very fine quality.

FURNACE FOR PRODUCING BLACK FROM PITCH, ROSIN, Etc.—An apparatus used in Germany consists of a chamber with a slanting outlet tube for the smoke, leading to the chamber where it is deposited, and a movable iron cover with a regulator for the air supply. The combustible material is placed in a pan at the bottom

of the chamber, whilst the exterior of the pan is cooled in another tray containing water, the object of this being to prevent the temperature rising too high and causing dry distillation to take place.

Large quantities of lamp-black, suitable for printing ink, are obtained by burning vaporised rosin (rosin gas) in lamps beneath a revolving cylinder containing water.

Dreyher's apparatus used for this process is shown in section in Fig. 54, and, as will be seen, is on the same principle as the apparatus

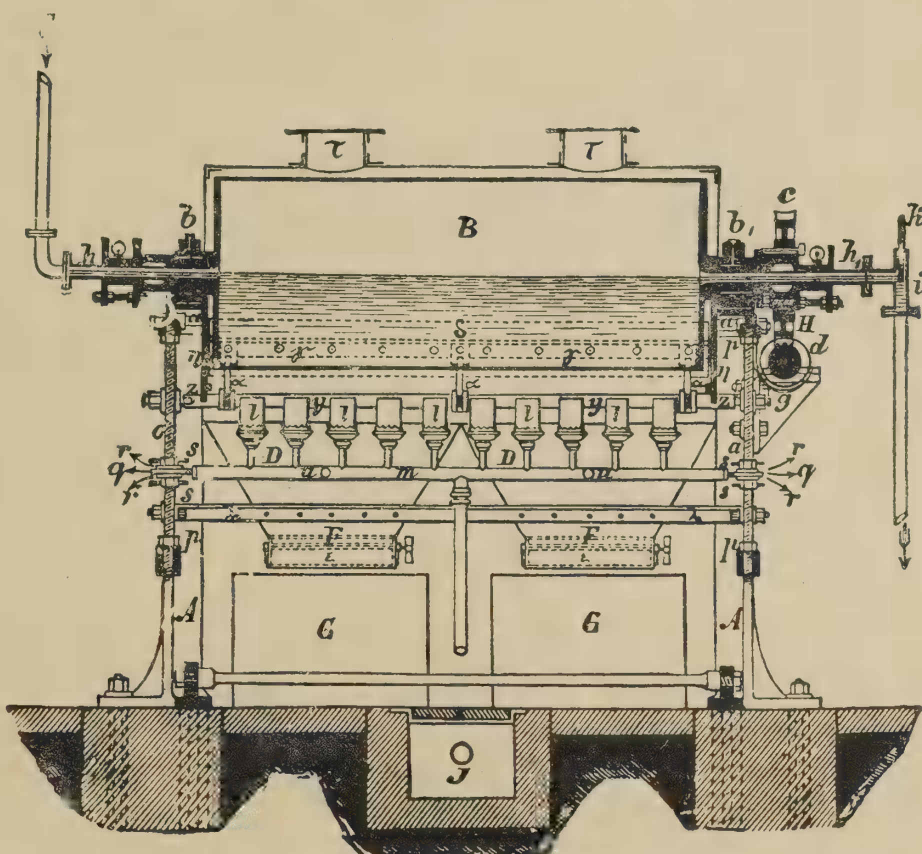

FIG. 54.—Dreyher's lamp-black apparatus.

illustrated in Fig. 53. The rosin gas is burned in the lamps *l*, *l*, *l* (Fig. 54), and the flames are chilled by the cylinder B. The lamp-black carried upwards by the combustion gases is deposited on iron catchers coated with flannel, and from these it is mechanically shaken into the boxes.

A type of apparatus for making the black from rosin is shown in Fig. 55, where V is a device for allowing the melted material H to fall on to the hot iron plate S, where it is burned in a limited supply of air.

In the apparatus patented by Lamp-black, Ltd., and Menzies (Eng. Pat., No. 17,233, 1912) the products of incomplete combustion from oil burners or sprays are condensed in a series of connected chambers, each of which has means for removing the lamp-black. These chambers may be connected in such a way that the combustion products pass through them in zig-zag fashion. Carbon dioxide may be removed by means of lime water, caustic soda solution, etc., and the spent gases are led back to the burners to form a fresh charge.

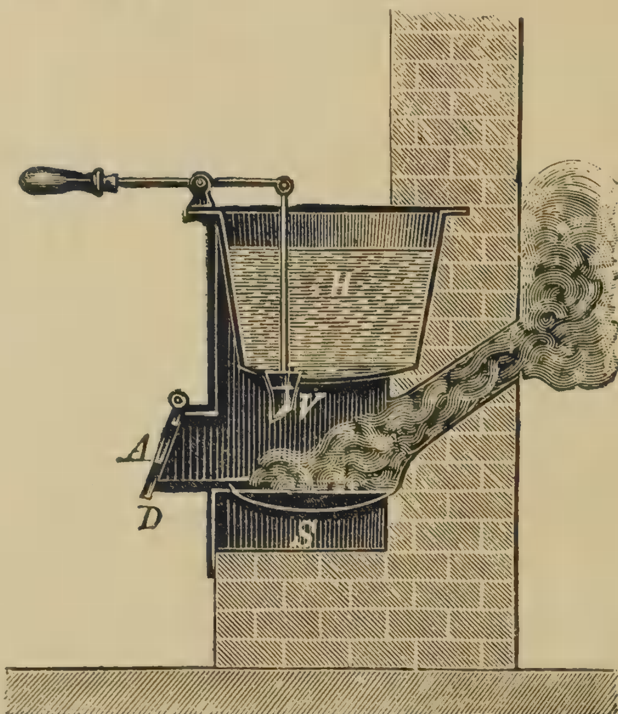

FIG. 55.—Apparatus for making lamp-black from rosin.

In *Bosch's* German Patent (1913) the lamp-black is carried through heated tubes to a vessel where it is submitted to centrifugal force. The resulting product is free from enclosed gases.

According to another patent of *Bosch*, acetylene is used as the source of the black, being introduced into the decomposition chamber through a rotating tube, which gives it a circular motion.

In a United States patent (No. 741,726, 1903) tar is heated to about 300° to 400° C., in a rotating cylindrical furnace, in which is a spiral ridge to conduct the tarry matter towards the outlet at one end, whilst the volatile products escape through a special opening.

OTHER BLACK PIGMENTS.—Numerous substitutes have been

proposed for lamp-black as a pigment in printing-ink, but not many of these have come into general use.

Vegetable black, formerly known as *Frankfort black*, *drop black*, or *vine black*, was originally prepared by heating vine twigs in closed crucibles, extracting the residue with water, drying the powder, mixing it with a weak solution of glue, and forming it into pear-shaped drops. It is now made by carbonising waste vegetable material such as spent tan bark, or raisin skins, in closed vessels.

This and other forms of charcoal have a granular character, whereas lamp-black is flocculent, and as no amount of grinding will effect thorough incorporation of such granular pigments with the varnish, they are unsuitable for good printing ink in which a granular material is not required.

To obtain a fine pigment from coal, jet, etc., *Child* and *Johnson* (Eng. Pat., No. 8532, 1909) drive the dust from the mills through successive chambers with baffles to retain the heavier particles.

Yeast Black.—The mixture of dead yeast and lees in wine, or the excess of fresh yeast in breweries, may be calcined in tubes to obtain a carbon that can be used as a pigment.

Bone black is made by a similar process, the bones being heated in a closed retort, and the largest proportion of mineral salts being subsequently extracted with an acid. The product is then known as "acid-washed bone black." Like vegetable black, it has a granular texture, which, however, makes it a suitable pigment for lithographic inks, for which gas black is unsuitable.

Mineral black is the commercial name of a product derived from carbonaceous shale. It is used in certain types of printing ink, in which a low degree of absorption of oil by the pigment is desired.

CARBON BLACKS.—The black pigment obtained by the deposition of the smoke from burning gas upon metallic surfaces is sold under various trade names, such as *gas black*, *peerless black*, *hydrocarbon black*, *silicate of carbon*, *jet black*, etc.

It was prepared on a small scale by certain manufacturers in this country from the ordinary gas supply of towns some forty years ago, but owing to its high price (5s. a pound) never came into general use. It was estimated that in 1921 the total output of carbon black in the United States was 58,632,000 lbs.

The discovery of natural gas in different parts of the United States put a cheap source of gas carbon at the manufacturers' disposal. *Cabot* * states that the first experiments with the natural gas were made in 1872 in Pennsylvania, and a factory was built to manufacture the pigment on a commercial scale. The first lot

* *Journ. Soc. Chem. Ind.*, 1894, xiii., 128.

was sold at about 10s. a pound, and the demand soon exceeded the supply. Other factories were established and the price rapidly fell, until in 1889 it was as low as 1½d., and several firms were ruined. Since then it has again risen in price, and now fetches more than the price of ordinary lamp-black.

The gas issues from borings about 2,000 feet in depth by 8 inches in diameter, and is burned in ordinary gas jets. In the earliest method of collecting the black flat-bottomed cast-iron pans were fixed above the jets, and the soot removed by means of travelling scrapers. Several United States patents were next taken out for processes in which the flame was made to impinge on revolving iron cylinders. In 1883 claim was made for a process in which a large plate with holes for ventilation was made to revolve over the burners, and the black removed by passing over a fixed scraper.

One method, introduced in 1883 by *Blood*, makes use of revolving small rotating discs as the surface for the deposit. These discs are grouped in rows of 21 units, with two or four rows per building, and there are usually about 1,532 discs in a large factory of 18 buildings.

In another process, also commercially successful, the deposition surface is kept stationary, while the gas jets and collecting box revolve beneath it.

In the " channel system " the gas is burned in a series of burners at a distance of 3 to 4 inches below steel channels, which are grouped in tables of eight. The black is deposited on the underside of these channels, to which a slow reciprocating motion is imparted, with the object of scraping off the deposit into hoppers. There is also what is termed the " roller or rotating cylinder process."

The yields obtained by these processes vary from about 0·2 to 3·5 lbs., according to the pressure of the gas, supply of air, and other conditions.

Carbon blacks are characterised by their intensity of tone, and the printing done with inks containing them has a rich glossy appearance. Owing to their being of a more granular character than lamp-black they are not so readily incorporated with the varnish, and were not looked upon with favour by English printers long after they had been extensively used in America. English manufacturers have since introduced rollers of chilled steel in place of granite for the grinding of carbon black inks, and their products can compete with those of American origin.*

Gas-black consists mainly of carbon, and has only traces of mineral matter. Samples analysed by *Cabot* (*loc. cit.*) contained 92 to 93 per

* Harding, *Process Year Book*, 1898, p. 65; 1902, p. 126.

cent. of carbon, 5 to 6 per cent. of oxygen, and 1 to 2 per cent. of hydrogen.

The following table embodies more recent analyses by *Selvig* :—*

GAS-BLACKS.

	†Long Black No. 1.	Long Black No. 2.	Long Black No. 3.	Short Black No. 1.	Short Black No. 2.	Short Black No. 3.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Moisture, . .	3·56	7·13	5·30	2·25	3·03	3·12
Volatile matter, .	11·99	13·41	10·40	5·60	5·48	5·58
Fixed carbon, .	84·40	79·44	84·16	92·13	91·47	91·22
Ash, . . .	0·05	0·02	0·14	0·02	0·03	0·08

Like lamp-black, impure gas-black is always contaminated with tarry oils, which can be removed by calcination (*infra*), leaving a residue containing 98 to 99 per cent. of carbon. Its tinctorial power is considerably higher than that of lamp-black, and it will impart a deep grey tone to 100 times its weight of white lead. It requires approximately twice as much varnish as lamp-black does to form an ink of the right consistence, and the ink thus dries more slowly.

Owing to its hygroscopic character, carbon-black must be stored in well-closed vessels, otherwise the water it absorbs forms globules with the oil, and interferes with the perfect incorporation.

Carbon-blacks are miscible with water, and this property affords a means of distinguishing them from lamp-black.

PURIFICATION OF LAMP-BLACK.—However carefully prepared, lamp-black, even after careful grading, has a more or less brownish tint, due to the presence of volatile, tarry, and oily matters derived from dry distillation of part of the organic substance used in the combustion. When these are eliminated, the residue consists of almost pure carbon, and is then deep black in tone.

* *Carbon Black—Its Manufacture, Properties, and Uses.* By R. O. Neal and G. S. J. Perrott. Bull. No. 192. U.S.A. Dept. of the Interior, Bureau of Mines. 1922, p. 72.

† The terms "length" and "shortness" are thus defined by Underwood (*The Chemistry and Technology of Printing Inks*) :—"If a pigment when mixed with a large quantity of oil still remains stiff or cannot be drawn out into a string between the fingers, but breaks, it is said to be short."

An ink that flows well must also have the property of being drawn out into a string between the fingers, and this is called "length."

Chemical Purification.—The technical method of removing the brown impurities is to boil the black with successive portions of strong caustic soda ley until only a faint colour is imparted on treating the substance with a new portion. The powder is then washed thoroughly, and appears deep black to the eye.

In order to remove all traces of impurities, however, it is necessary to continue the boiling with caustic soda until a colourless extract is obtained, and subsequently to boil the residue with *aqua regia* until nothing more dissolves. The final product, after washing with water, is a deep black, very friable powder. It is practically pure carbon, and emits no smell when burnt. The cost of handling the material so many times is too great to permit of chemical purification being used in the preparation of any but the very finest and most expensive grades of lamp-black (*Andés*).

According to a recent German patent of *Dieffenbach* and *Moldenhauer*, the lamp-black is treated with an oxidising agent such as chlorine, an alkali hypochlorite, permanganates, chromates, ferric chloride, etc.

Purification by Calcining.—The brown tarry oils and other impurities in lamp-black can be expelled by heating the crude product to a sufficient temperature to volatilise them. In this process it is essential to prevent any air coming into contact with the hot carbon, which in that case would be partially burned into oxides of carbon; and also to avoid overheating, the result of which is to cause the lamp-black to cake into lumps, which are very difficult to distribute uniformly through the lithographic varnish.

The apparatus used for the calcination is a cast-iron box, in the cover of which a small opening is left to allow the volatile impurities to escape. The outside of this box is coated with a thick layer of clay to protect the metal from oxidation, and the juncture of the cover is carefully luted with the same material. Every precaution is taken to avoid the slightest opening into the box, with the exception of the small one in the cover.

After being charged with the crude lamp-black, the box is placed in a suitable furnace and heated gradually from behind until the whole has attained a bright red heat. It is kept at this temperature for about thirty minutes, and then removed from the furnace and cooled in a current of air, the opening in the cover being protected from the possible admission of atmospheric oxygen by having a piece of glowing charcoal placed over it. The box is not opened until quite cold, lest any oxidation of the carbon might take place. To obtain an absolutely black product, it is often necessary to repeat the calcining as many as six times or more. According to

Irvine the loss in weight on calcining lamp-black is upwards of 15 per cent.

COMPOSITION OF LAMP-BLACKS.—After careful purification lamp-blacks consist of 96 to 98 per cent. of carbon, and contain very little mineral or oily products.

The following analyses of four pure samples of lamp-black were made by *Stillwell* and *Gladding* * :—

	1. Per cent.	2. Per cent.	3. Per cent.	4. Per cent.
Carbon	97.38	97.38	96.24	96.13
Mineral matter (ash) . .	0.05	0.05	0.03	0.23
Moisture (loss at 100° C.) .	0.07	0.08	0.03	0.04
Volatile substances . .	2.50	2.50	3.70	3.60

A commercial sample of impure lamp-black examined by us gave the following results :—Ash, 0·29 ; oily matter (ether extract), 8·12 ; and total nitrogen, 0·76 per cent.

Analyses of various lamp-blacks and other blacks by *Selvig* (*loc. cit.*) gave the following results :—

	Lamp-black.		Bone Black.	Vine black.	Wood-Pulp black.	Carbon from cracking of the Threads.	
	1. Per cent.	2. Per cent.	Per cent.	Per cent.	Per cent.	1. Per cent.	2. Per cent.
Moisture, .	0·39	3·12	3·88	9·58	6·42	0·02	1·25
Volatile matter,	2·26	17·38	10·92	29·54	9·78	0·78	6·40
Fixed carbon, .	97·35	79·44	2·68	40·50	78·84	98·36	92·11
Ash, . .	0·00	0·06	82·52	20·38	4·96	0·84	0·24

Methods of Examining Lamp-Blacks and Gas-Blacks.

In judging of the suitability of a black for printing ink, the main points to be taken into consideration are the intensity and permanence of its blackness, its tinctorial power, the fineness of its particles, and its freedom from any considerable proportion of oily impurities and mineral matter.

* *Process Year Book*, 1901, p. 141.

Moisture.—One gramme of black is heated for an hour at 105° C. in an oven. Most blacks contain 2 to 4 per cent. of moisture, although some may contain as much as 7 per cent. Some blacks will absorb as much as 15 per cent. of moisture from the air (*Perrott*).

Estimation of Mineral Matter.—A weighed quantity (about 0·3 grm.) of the powder is ignited in a weighed platinum basin over a small Argand flame, and the residue weighed when burned completely white. The best qualities of lamp-black contain only traces of ash (*cf.* "Analyses" *supra*).

Tarry Oils.—It has been pointed out by *Irvine* * that the halo to be observed round the letters in some old books and papers is to be attributed to the presence of tarry compounds, such as pyrene and chrysene, in the black.

For the estimation of such impurities, 2 or 3 grms. of the sample are extracted with ether, the extract evaporated, and the residue weighed. A specimen of lamp-black examined by us in this way yielded 8·12 per cent. of a dark yellow viscid oil, with a strong empyreumatic odour and a bitter taste. *Smith* † advocates the following qualitative test :—A pinch of the powder is put on a piece of filter paper and moistened with a few drops of ether, which will dissolve any oil present and then leave a brown or yellow stain surrounding the powder.

Acetone Extract.—Two grms. of the black are extracted with 20 c.c. of acetone for one hour in a Soxhlet extractor, and the weight of the extract determined. The extract for a pure carbon black is usually *nil* (*Perrott, loc. cit.*).

Alkalinity or Acidity.—Free alkali or acid, which may be left by the process of purification, may react with other constituents of the ink and lead to loss of colour.

Free alkali is detected by boiling 0·1 grm. of the black with 10 c.c. of water, filtering, and adding a drop of phenolphthalein solution to the filtrate (pink colour). If, on the other hand, the aqueous extract is acid, it will remain colourless on the addition of the phenolphthalein, and will require the addition of alkali solution to produce the pink colour.

Degree of Fineness.—Lamp-black consists of foliated particles, whilst gas-black is finely granular in character, and vegetable charcoals (Frankfort black, etc.) still more granular. A practical test for comparing an unknown sample with one of known fineness is to mix equal weights of the powders with equal quantities of varnish, and to spread the mixtures in thin layers on glass. When

* *Journ. Soc. Chem. Ind.*, 1894, xiii., 131.

† *Process Year Book*, 1903, p. 137.

the glass is held to a strong light, the layer of fine black will be found impervious to the light, whilst the particles of the coarse black allow the light to pass.

An ingenious adaptation of the physiological method of counting the corpuscles in blood to the valuation of pigments has been devised by *Kühn*.* The finely powdered material (1 grm.) is mechanically shaken for 15 minutes with a measured quantity (10 c.c.) of a suitable medium such as glycerin or linseed oil. A minute quantity (0·01 c.c.) is then withdrawn by means of a micro-pipette, diluted to 1 c.c. with the medium, and again shaken for 15 minutes, after which one drop is transferred to the object glass of a Zeiss-Thoma chamber, as used for counting blood corpuscles, covered with a cover-glass, and the number of particles counted (after 1 to 12 hours) under a magnification of 550 diameters. Duplicate results should agree within 1 per cent.

In this way 1 grm. of heavy spar was found to contain 4·5 milliards of particles. After regrinding the number rose to 12 milliards, and after a third grinding to 18·4 milliards. A sample of lamp-black with a specific gravity of 1·57 contained 960 milliards of particles per grm. Hence an average particle was calculated to have a diameter of 10·8μ and to contain 26 milliard molecules of carbon.

Microscopical Examination.—According to *Perrott* (*loc. cit.*, p. 78), the average size of the particles of carbon black is about 100 millimicrons, the particles of "long" blacks being slightly larger than those of "short" blacks. Well calcined lamp-blacks are more opaque than carbon blacks.

Mixtures of thin lithographic varnish with long or short blacks at first appear exactly alike, but after a few minutes a pronounced difference can be seen. The short black begins to agglomerate into groups of 20 to 30 particles and, after about an hour, more than a hundred may be thus grouped together. The long black, however, remains completely dispersed after several hours.

Lamp-black shows this tendency to agglomerate as much as do short blacks, and lamp-blacks usually make "long" inks.

Intensity.—The above method of testing the fineness of the particles is also frequently employed for comparing the intensity of the tone of two samples; but *Smith* (*loc. cit.*) objects to it on the ground that in the case of shale-blacks the oil varnish may rise to the surface, and the layer thus appear to be blacker than it really is. He, therefore, advocates making the comparative tests on wood instead of glass, under parallel conditions.

Permanence.—Apart from the results obtained in actual practice,

* *Zeit. angew. Chem.*, 1915, xxviii., 126.

which obviously take time, *Smith* recommends testing the blacks with sulphuric acid and with solutions of sodium hydroxide and ammonia. Effervescence with the acid indicates the presence of carbonate, whilst if the blackness is at all fugitive, the pigment, when dried after treatment with alkali, may show a loss in intensity.

Tinctorial Power.—A paste is prepared by adding linseed oil to a mixture of 0·1 grm. of the black with 8 grms. of white lead, and after thorough incorporation spread upon glass, and the tint compared with that given by a standard sample of lamp-black under the same conditions.

Colour.—This term is used to indicate the relative blackness of the black when mixed with oil. In each case 0·3 grm. of the sample is mixed with 1·3 c.c. of refined linseed oil (added from a burette), the mixtures spread with a palette knife, side by side, on a glass slip, and the relative colours compared by viewing them from above (*Perrott*).

Opacity Test for Covering Power.—A mixture of 0·1 grm. of the powder, and 1 c.c. of oil is spread in a uniform layer over paper until the surface below becomes visible, the areas of paper covered by equal weights of two pigments thus affording a measure of their relative opacity. In some cases an additional amount of oil must be added to the mixture to enable it to be spread out to its maximum extent, so that the total amount of oil used may also be taken as a measure of the covering power.

Distinction between Lamp-blacks and Gas-blacks.—*Cabot* (*loc. cit.*) has based a distinguishing test on the fact that gas-black can be readily mixed with water (p. 213).

Specifications for Carbon Blacks.—The following specifications are suggested by *Perrott* * for carbon black for printing inks :—Moisture, less than 5·0 per cent. ; ash, less than 0·1 per cent. ; acetone extract, less than 0·1 per cent. The colour and tinting strength must equal that of a selected standard, and the black must be free from grit.

Mixing the Black and Varnish.

PROPORTION OF BLACK TO VARNISH.—This will obviously depend to a large extent on the character of the printing for which the ink is required, as well as on the quality and nature of the pigment used. Thus for newspaper work a very different kind of ink is required than is the case for fine book work and illustrations.

* *Carbon Black.* *Bull.* 192. Dept. of Interior, U.S.A., Bureau of Mines, 1922, p. 65.

According to *Andés*,* the proportion of lamp-black or other black in German printing ink ranges from about 20 to 40 per cent., a little blue pigment (indigo, aniline dye-stuffs, etc.) being added to the best qualities of ink.

He gives the following proportions as typical of inks in common use :—

	Ink for Rotary Machines.	Common Newspaper Ink.	Book Ink.	Ink for Illustrations.	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Oil Varnish .	70–72	76–78	77–79	78	78
Lamp-black .	30–28	24–22	23–21	20	19
Paris Blue . .	—	—	—	2	2
Indigo . .	—	—	—	—	1

MIXING THE VARNISH AND LAMP-BLACK.—In some of the old foreign methods of mixing the pigment with the oil varnish, the ink was only incorporated by the pressman on the inking-stone immediately before use (see p. 193). As a thorough admixture of the ink was a tedious process, the old English ink manufacturers were in the habit of preparing a complete product, though, according to *Moxon* (*loc. cit.*), the results given by this ink were inferior to the Dutch printing ink. The mixing of the ingredients was effected by stirring them together in a vessel, and subsequently grinding them on a stone with a muller. Owing to the very light and dusty nature of the lamp-black, the incorporation is now usually effected in a mixing machine, several types of which are in use.

Quack's Mixing Machine.—This is a simple and effective apparatus, consisting of a closed vertical cylinder with rounded bottom, in which revolve two interlapping flat rings, which scrape the sides of the vessel and effect a thorough admixture of the contents. The cylinder is supported outside by axles, so that it can be easily inverted to remove the ink.

Fig. 56 shows the mixing apparatus viewed from above.

Werner and Pfleiderer's Mixing Machine.—These are made in various sizes to take charges of ½ to 1,400 kilos. They are constructed in the form of a horizontal cylinder, mounted on axles so as to be readily emptied, and the incorporation of the varnish and lamp-black is effected by means of revolving paddles.

* *Oel und Buchdruckfarben*, 1889, p. 236.

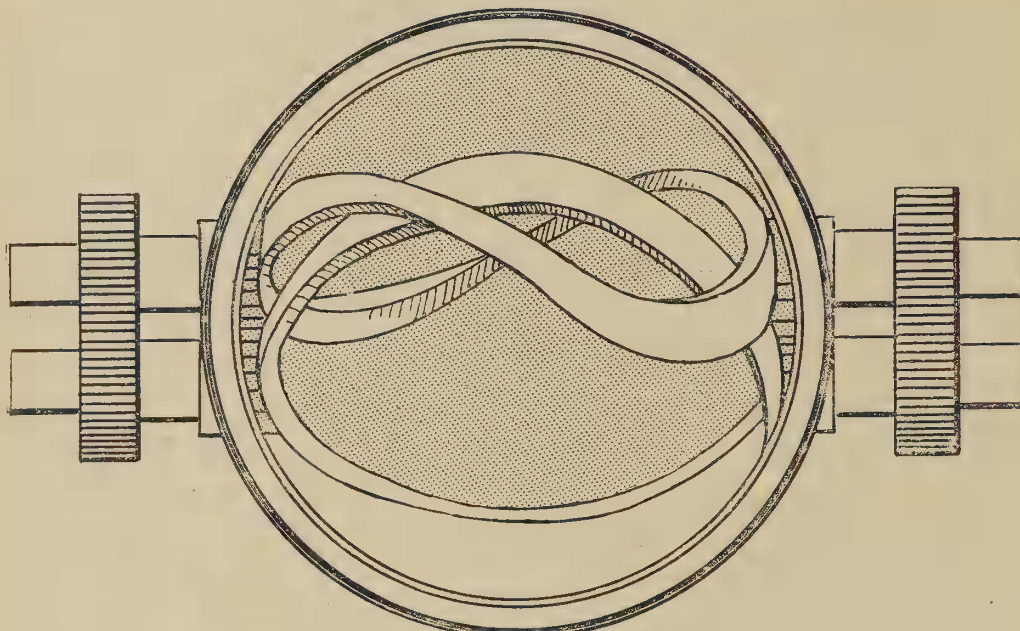

FIG. 56.—Quack's Mixing Machine.

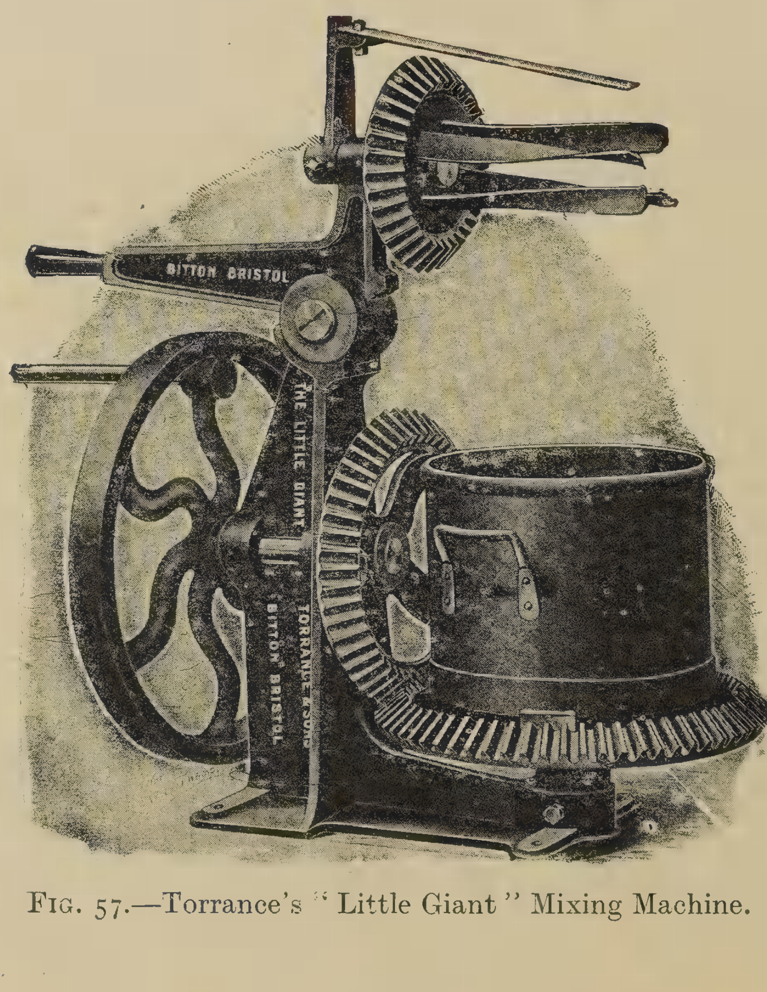

FIG. 57.—Torrance's "Little Giant" Mixing Machine.

Torrance's "Little Giant" Mixer.—This machine, which takes a charge of 5 gallons, is extensively used by ink manufacturers for mixing small quantities of any particular ink. As shown in Fig. 57 it is worked by hand, and can be moved to any desired place. The mixing is effected by means of rotating blades, which are brought into position in the pan by raising the lever.

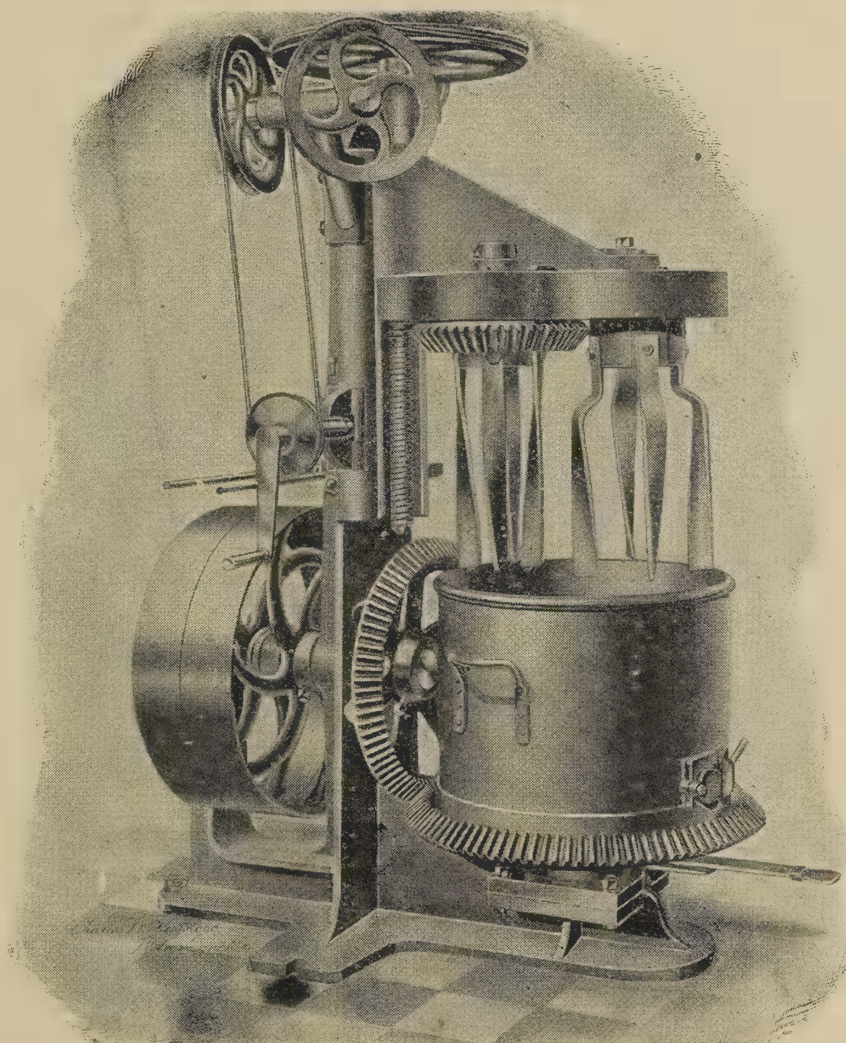

FIG. 58.—Torrance's "Patent" Mixer.

The Torrance "Patent" Mixer.—Fig. 58 shows one of these machines, which is worked upon the same principle as the hand machine, but with two sets of blades in the revolving pan. By moving a lever the pan is made stationary, while the blades continue to revolve and effect thorough and uniform admixture of the ink. From 4 to 5 horse-power is required for driving the machine. The

mixing is very rapidly done, but the output will obviously depend upon the consistence of the mixture of pigment and varnish.

Grinding.

After thorough admixture in a mixing machine, as described in the preceding pages, the *pulp* of printing ink requires grinding

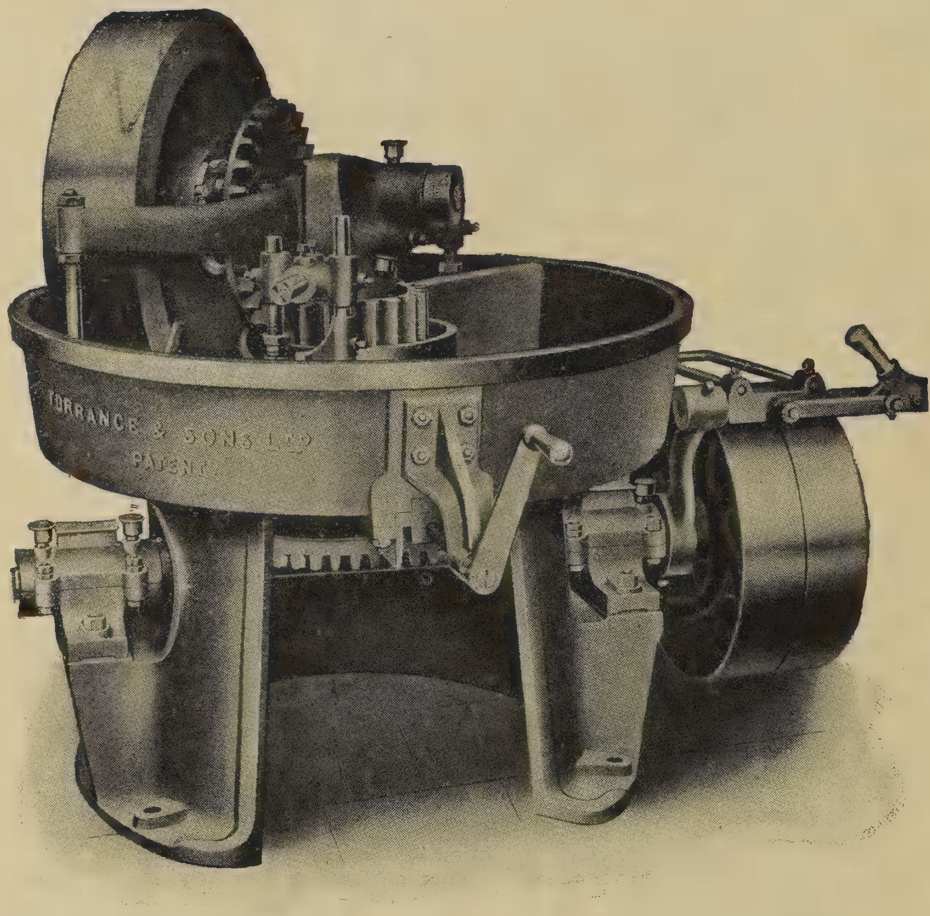

Fig. 59.—The "Torrance" Mill.

between rollers, so as to reduce it to an absolutely homogeneous mixture free from all lumps. For this purpose it is transferred from the mixer to a mill, in which it is passed between rollers of fine-grained hard stone such as porphyry, one grinding in a mill with six or nine rollers being usually sufficient if the material has been properly mixed.

For grinding granular pigment such as gas-black, machines with rollers of chilled steel are used in America and more recently in England.

The "Torrance" Mill.—This is made in various sizes up to a diameter of 8 feet, the size (12-inch) shown in Fig. 59 being the one

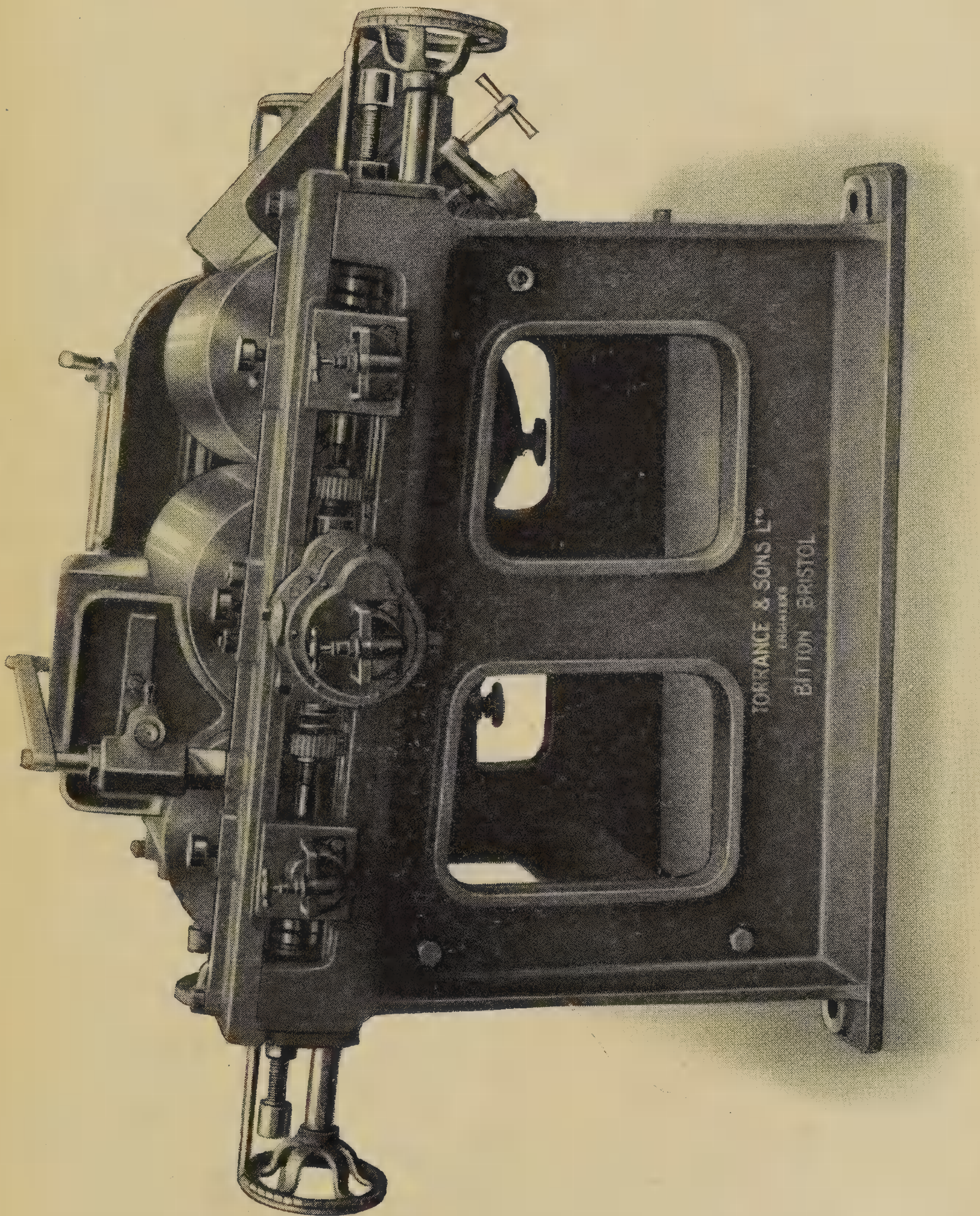

FIG. 60.—Torrance's "Silent Quadrant" Mill, with micro-adjustment gear to the rolls.

most in demand for the mixing and partial grinding of moderate quantities of ink. The steel roller is highly finished, and special scrapers are in constant contact with the interior of the pan and

the surface of the roller. About 4 horse-power is required for driving the machine.

Torrance's "Silent Quadrant" Mill.—For the final grinding of the finest qualities of printing ink a machine of the type shown in Fig. 60 is employed. This has rollers of fine hard colonial granite which, owing to an ingenious arrangement of quadrants, are constantly adjusted in their positions towards each other as they become worn, thus avoiding the necessity of having to replace one of them by a smaller roller.

The gearing is enclosed in an oil-box (shown open in the illustration), thus ensuring a minimum of friction and silence in working. Another special feature of the machine is that the scraper or "doctor" is attached to the neck of the roller bearings, so that it always stands in the same relative position towards the roller.

In some of these machines rollers of chilled iron, cooled with water, are substituted for the granite rollers, and this is an advantage for some kinds of ink, since it neutralises the effect of the heat caused by the friction.

The machine is made in various sizes, with rollers ranging from 7 to 16 inches in diameter.

In *Neal's* grinding mill (Eng. Pat., No. 2,640, 1860) the bottom roller alone revolves, whilst the top one is fixed.

A grinding mill patented by *Jackson* (Eng. Pat., No. 957, 1870) contains flat circular grinding plates which revolve on a vertical spindle. On the surface of these plates are teeth, whose cutting faces are arranged half in one direction and half in the other, so that by reversing the motion from time to time half of the teeth are sharpened whilst the others are in action. The plates are kept cool by means of air-chambers between the fixed and revolving discs.

In a machine protected by *Kingdon* (Eng. Pat., No. 3598, 1873) the rollers were made to revolve in opposite directions, and the upper roller was much smaller than the lower. This arrangement was intended to accelerate the passage of the ink and prevent the darkening that sometimes occurs in grinding coloured inks.

Several recent patents are embodied in the Torrance Mills described above.

LITHOGRAPHIC INK.—Printing ink for lithography is supplied in tins, the price ranging from 4s. to 50s. per lb. A fair quality of black ink can be obtained for about 8s. per lb., and it does not deteriorate on keeping. It is in the form of a solid of the consistence of cold wax, and must be thinned down with varnish before it can be used for printing. A small quantity of ink is treated at a time, the varnish being added to it in minute quantities and rubbed down with the palette-knife. The ink is at first difficult to mix with

the varnish, but when a little has been incorporated with it it will readily absorb more. A good deal of practice is necessary before the lithographic printer can master the initial difficulties of reducing the ink to a printable condition. He must be guided to a great extent in dilution of the ink by the state of the atmosphere and the temperature.

The lithographer in a small way of business is frequently called upon to print such small things as concert programmes and the like in fancy colours, and must know how to compound inks of different hues. By the aid of a stone, muller, palette-knife, and varnish he should find no difficulty in accomplishing the work. The pigment or pigments employed are rubbed down in small quantities with the palette-knife and with medium or thin varnish, or with a mixture of the two, according to the state of the thermometer. He then grinds the mixture with the muller, gathering it up again with the knife and regrinding again and again. More colour is added as the operation proceeds, and as the ink gradually gains in thickness it will become necessary to do this by scattering the pigment over the stone, and grinding down with the muller without the intervention of the palette-knife. But the knife must be employed to scrape the colour from the stone, pile it up before submitting it again to the action of the muller. Ink thus prepared works better if kept for a day or two before being used.

Schweitzer * gives the following recipe of a German lithographic ink :—Bleached beeswax, 80; white grain (tallow) soap, 20; shellac, 20; and finest lamp-black, 20 to 25 lbs. The soap must be as free from water as possible. Fat, usually mutton tallow, is frequently a constituent of German inks.

The following examples of the composition—in lbs.—of six English lithographic inks are also given by *Schweitzer*:—

	1	2	3	4	5	6
Yellow wax . . .	40	—	140	18	6	100
Mastic	10	60	—	24	6	—
Gum lac	22	—	100	—	—	—
Tallow-soap . . .	22	60	70	18	6	100
Lamp-black . . .	9	50	32	15	3	50
Shellac	—	300	—	36	30	100
Soda-ash	—	60	—	—	6	50
Tallow	—	—	—	18	—	50
Turpentine . . .	—	—	—	3	—	—
Rosin	—	—	10	—	—	—

* *Loc. cit.*, p. 171.

LITHOGRAPHIC CHALKS.—These must have the same properties as lithographic inks of resisting the action of the acid upon the stone, and of being subsequently easily removed. They have a similar composition, but require moulding so that they can be sharpened. The following four recipes for preparing them are given by *Schweitzer*:—

For Strong Etching.

Wax,	64	64
Oil-soap,	22	48
Tallow,	24	..
Nitre,	2	3
Lamp-black,	15	24
Spermaceti,	..	32
Shellac,	..	16

For Weak Etching.

Wax,	50	60
Shellac,	35	25
Soap,	35	45
Soda,	5	5
Tallow,	5	10
Lamp-black,	20	20

For delicate tints, as in painting with opaque pigments, it is necessary to incorporate with the colour a considerable body of white, and for this purpose there is nothing better than zinc oxide. It is true that white lead has more covering power, but there is considerable risk of chemical change occurring when it is mixed with certain other pigments. A transparent alumina introduced by Messrs. *Madderton and Co.* affords an excellent means (in conjunction with oil) of rendering a coloured ink paler without changing its consistence. In chromo-lithography an ink is sometimes employed for a pale tint, or for enriching a colour already printed, in the same way that a water-colour is used by a painter; that is to say, the ink is sufficiently thinned down by varnish to make the paper show through it. This device has the advantage of reducing the number of separate printings and so saving expense. It is not applicable to printing from type. It is almost unnecessary to state that in printing establishments where a large amount of colour work is done, the inks are ground in mills, or are supplied ready compounded.

COLLOTYPE INK.—The usual practice of the collotypist is to rub down lithographic chalk ink with "middle" varnish, turpentine, and olive oil, and when he requires inks of different colours, he mixes each severally with a little turpentine before incorporation with the

other media. It is also customary to add to black inks a small proportion of Prussian blue, indigo, or Venetian red to improve the tone. A special inking slab and muller are used for each colour.

Schnauss * gives definite directions for preparing ink for collotype work on these lines. From our own experiments we can affirm that much depends in the collotype process upon the thorough incorporation of the ingredients of the ink, upon its even distribution, and upon the degree of moisture in the atmosphere, which has an influence upon the gelatin surface.

ROTAGRAVURE INKS.—In the "rotagravure" process both the press matter and the illustrations are printed simultaneously on a rotary machine while running at a high speed. Essentially the principle of the process is the reverse of that used in half-tone work, in which the printing surface is made up of an immense number of minute dots, which are large and touching one another in the shadows and minute and dispersed in the high lights.

In the rotagravure process, however, the printing surface is an intaglio composed of minute rectangular cells of varying depths. These cells, which number approximately 40,000 to the square inch, are filled with the ink, the excess of which is removed from the surrounding margins by means of a steel blade or "doctor," so that films of graduated depths are left in the cells on the cylinder. When the web of paper is now pressed against the mouths of these cells by the action of the impression roller the ink is lifted from the cells and transferred to the surface of the paper, the intensity of the deposited pigment corresponding with the amount of ink in the respective cells.

The ink for this process must have special characteristics quite distinct from those of ordinary printing ink. Thus it must be capable of being removed completely from the cells, it must not contain pigments which will yield deposits, it must not dry up in the cells, and it must be transparent without being excessively so.

These requirements have been met by using special media containing a balanced proportion of fixed and volatile ingredients, and by the use of pigments which, when properly incorporated with the varnish, are free from the defects just mentioned.

Thorough grinding of the pigment and medium is absolutely essential, and, in practice, it was soon found that the ordinary mills of the type described on the preceding pages were quite unsuitable for the purpose, owing to the fact that the volatile portion of the liquid medium evaporated too rapidly during the time

* *Collotype*, p. 56.

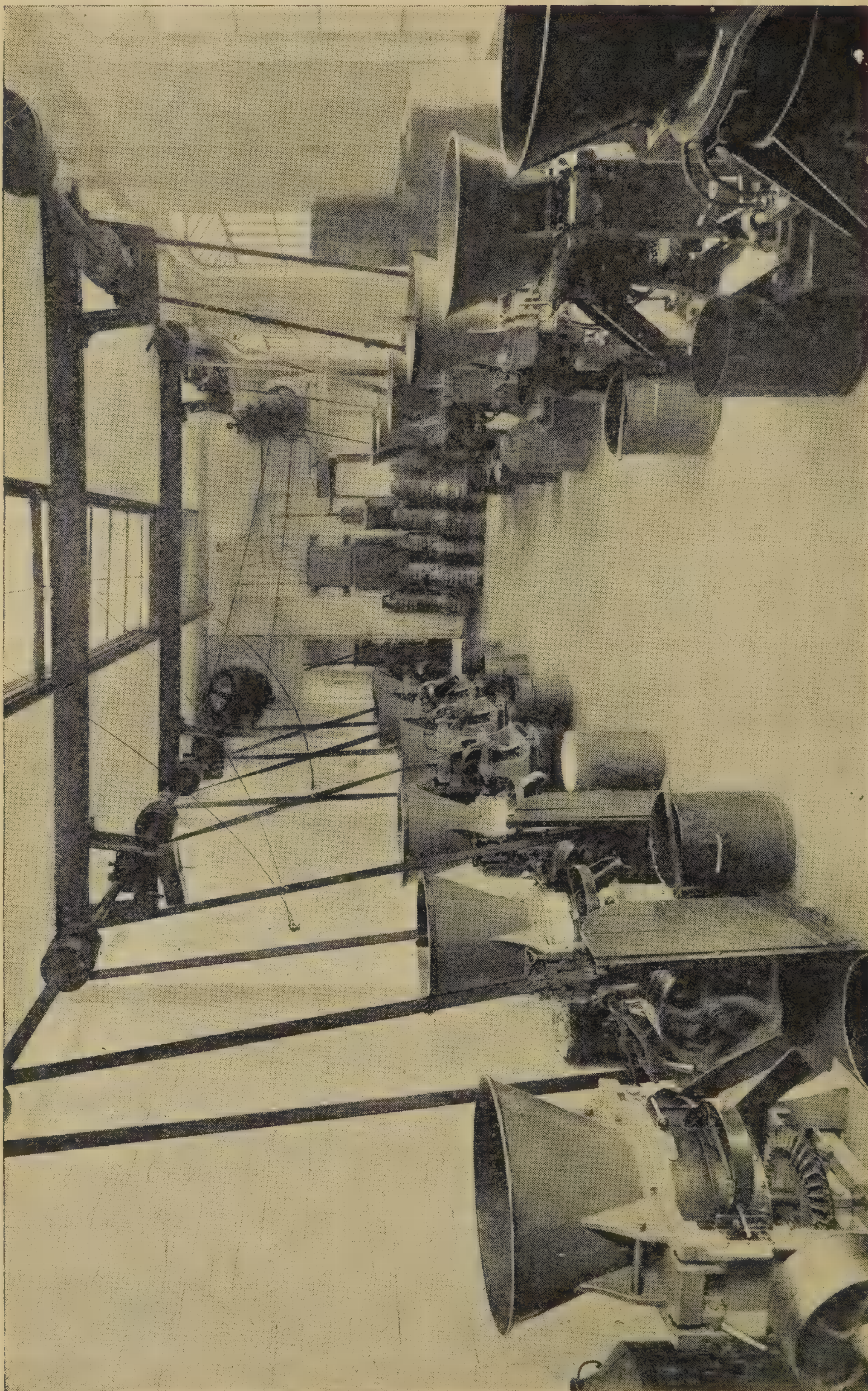

FIG. 61.—Mills for grinding rotagravure inks.

required for the grinding. It was, therefore, necessary to construct a special form of mill for these inks ; on p. 228 is shown two groups in a series of those used for this purpose by Messrs. *B. Winstone & Sons*, to whom the writer is also indebted for particulars of this interesting development in the history of printing.

These mills are in the form of a cone, and each contains two horizontal steel discs, one revolves above the other, and grind the ink into an absolutely uniform mass. It is most essential that there should not be a particle of gritty matter in the ink, since otherwise the highly polished surface of the cylinder may be scratched when the doctor blade is drawn across, with the result that an unwanted mark will be made on every impression on the paper.

To prevent the cylinder being ruined in this way, the greatest care is taken that no foreign matter shall find its way into the ink, and for this reason it is customary for printers to pass the ink through a hair sieve before using it in their machines.

LUMINOUS PRINTING INK.—A U.S. patent of *Krapp* (No. 1,097,981, 1914) describes a printing ink containing colloidal radio-active material and metallic sulphide incorporated with burnt oil, rosin, and soap.

CHAPTER XI.

COLOURED PRINTING INKS.

CONTENTS.—Early methods—Manufactured inks—Painters' pigments—Early ignorance as to proper pigments—Half-tone process block—Necessity for cleanliness—Overlays—Coarse-grain screens—Theory of colour—Diagrams of colour—Peculiarities of pigments—Permanency of pigments—Methods of testing permanency—Fast aniline pigments—Yellow pigments—Red pigments—Blue pigments—Green pigments—Purple and orange pigments—Brown pigments—"Art" shades—Tests of opacity and covering power—**Three-colour Printing**—Photographic falsification of colour—Coloured screens—Clerk-Maxwell's work—Colour screens or filters—Coloured light—Pure pigments unknown—General considerations—Examination of trichromatic prints—The half-tone dot—Necessity for transparent inks—Opacity of yellow pigments—Supplementary key block—**Inks for cheques and bank notes**—Patent inks for cheques—**Analysis of printing inks.**

EARLY METHODS.—Interesting details as to the use of coloured inks in printing in the early part of the last century may be gleaned from the large volume by *Savage*.* This contains many illustrations in colour, with a specimen block of each pigment employed. These are useful as witnesses of permanence, but the fact must be taken into consideration that these specimen tints have not been exposed to the action of light. Among the colours illustrated we find bistre, sepia, smalt, cobalt, and some others which are now seldom employed by the ink manufacturer.

It is worthy of notice that *Savage* makes no allusion to the purchase of coloured inks, and we may presume, therefore, that up to the date of this book, and possibly some time afterwards, printers were dependent for these upon their own resources.

MANUFACTURED INKS.—A later author, *Ringwalt*,† remarks that "in the present advanced state of ink-making" it is better for printers to rely upon the manufactured article than to attempt to make their own inks. And he suggests that the difficulty of reducing these inks and mixing them with varnish in the best way to meet the necessities of the work in hand, is quite enough in itself,

* *Practical Hints on Decorative Printing*, 1822.

† *The American Encyclopædia of Printing.* Philadelphia, 1871.

without the trouble of compounding the inks being added to it. If, however, the printer should insist on being independent in this matter he is referred to *Houghton's* book * for further information on the subject of ink-making.

Referring to *Houghton*, we find that he admits that coloured inks can be purchased ready for use, but complains that they are dear, and that the required tints cannot always be readily obtained. He advises the printer, therefore, to buy his own raw materials and to mix them for himself—taking care that the colours employed are of the best. The appliances and materials necessary consist of a muller, a marble slab and palette-knife, a can of printer's varnish and the raw colours. He then gives a review of the best colours to use.

PAINTER'S PIGMENTS.—We may take it as a general rule that pigments used by painters can, with very few exceptions, be adapted to the printing-press, always remembering that the painter is not limited to a certain thickness of material. He can if he likes, and as many do, pile on the paint with a palette knife so that it lies on the canvas in prominent ridges. The printer, on the other hand, must use his colours in such thin layers that their thickness cannot be measured even by a micrometer. It is obvious that this means that the pigment used must have great body or covering power, unless it is intended by printing one colour above another to get a compound tint.

EARLY IGNORANCE AS TO PROPER PIGMENTS.—In a book † by *Savage* of later date than his large volume a chapter is devoted to coloured inks, in which he deplores the ignorance of printers and ink-makers concerning colours and their application to the press. He advises the use of slab and muller, and good printing ink varnish, and in cases where the ink shows a tendency to accumulate upon the type recommends the addition of curd soap—which must be rubbed into the ink with the muller. He then repeats in slightly amplified form the particulars of the different pigments which he gives in his previous work. It is interesting to note that he advocates the use of carmine for a crimson ink, but only for very particular purposes, adding naïvely, "I have been accustomed to pay for the best two guineas an ounce."

THE HALF-TONE PROCESS BLOCK.—The introduction of the half-tone photographic process block, which has largely superseded the art of wood engraving, caused quite a revolution in printing methods. The etched dots upon these blocks are so fine in character that the work is comparable with a steel engraving rather than with

* *Printer's Everyday Book*, 1856.

† *On the Preparation of Printing Ink both Black and Coloured*, 1832.

one upon wood; and if one cares to look up the files of any illustrated journal of the period when these blocks came into use, he will see what deplorable things the printers made of them. Neither the paper nor the ink was good enough to meet the needs of these finely etched blocks; and although we must regret the decline of the beautiful art of wood-engraving, we must put to the credit of the process block a revival of the printer's art which has been beneficial from every point of view.

NECESSITY FOR CLEANLINESS.—Printers have learned that under the new conditions cleanliness, as well as care, is needed at every stage of the work. When type and electros from comparatively coarse wood-cuts, both of which were treated with black ink only, were the sole requisites of the printer's art, the workshop was the home of grime, perhaps necessarily so. But now that the work entails the employment of delicately etched process blocks, much greater care is needed. The place must not only be kept scrupulously clean, but a uniform temperature must be maintained if good work is to be produced. The common use of the electric motor for driving the machinery has banished most of the dirt; and the question of temperature is not a difficult one to solve. The black ink used for process blocks must be of the finest description, and it is found in practice that they take up far less ink than either type or wood-cuts. The layer of ink is so very thin that it is a matter of necessity that it should have good covering power; otherwise the impression will appear to be grey and flat.

OVERLAYS.—These blocks require to have the pressure so adjusted that it is greatest in the shadows, less in the half-tone, and lightest of all in the high lights. This desideratum is secured by overlays, and a great improvement was effected by the introduction of an overlay made of guttapercha on paper, which was produced by a photographic process. This overlay, which is specially adapted to the process block, was introduced from America and is known by a patent name.

COARSE-GRAIN SCREENS.—In the case of rapidly printed newspapers on rotary machines, half-tone blocks made with coarse-grain screens are coming more into use every day and displacing the line-drawing; and it is often found advisable to use a finer grade of ink for the pages bearing the illustrations than for those containing the text. In certain illustrated journals it is customary to print fine-grain half-tone blocks in coloured ink while the accompanying text is in black. This, of course, involves separate printing unless a two-colour machine is employed.

THEORY OF COLOUR.—It would be beyond the scope of this

work to devote much space to the theory of colour, although we are fully alive to the undoubted advantages to be secured by all those having to deal with colour, from an understanding of the principles upon which that theory is based. There are so many excellent manuals upon the theory of colour, the harmony of colours,

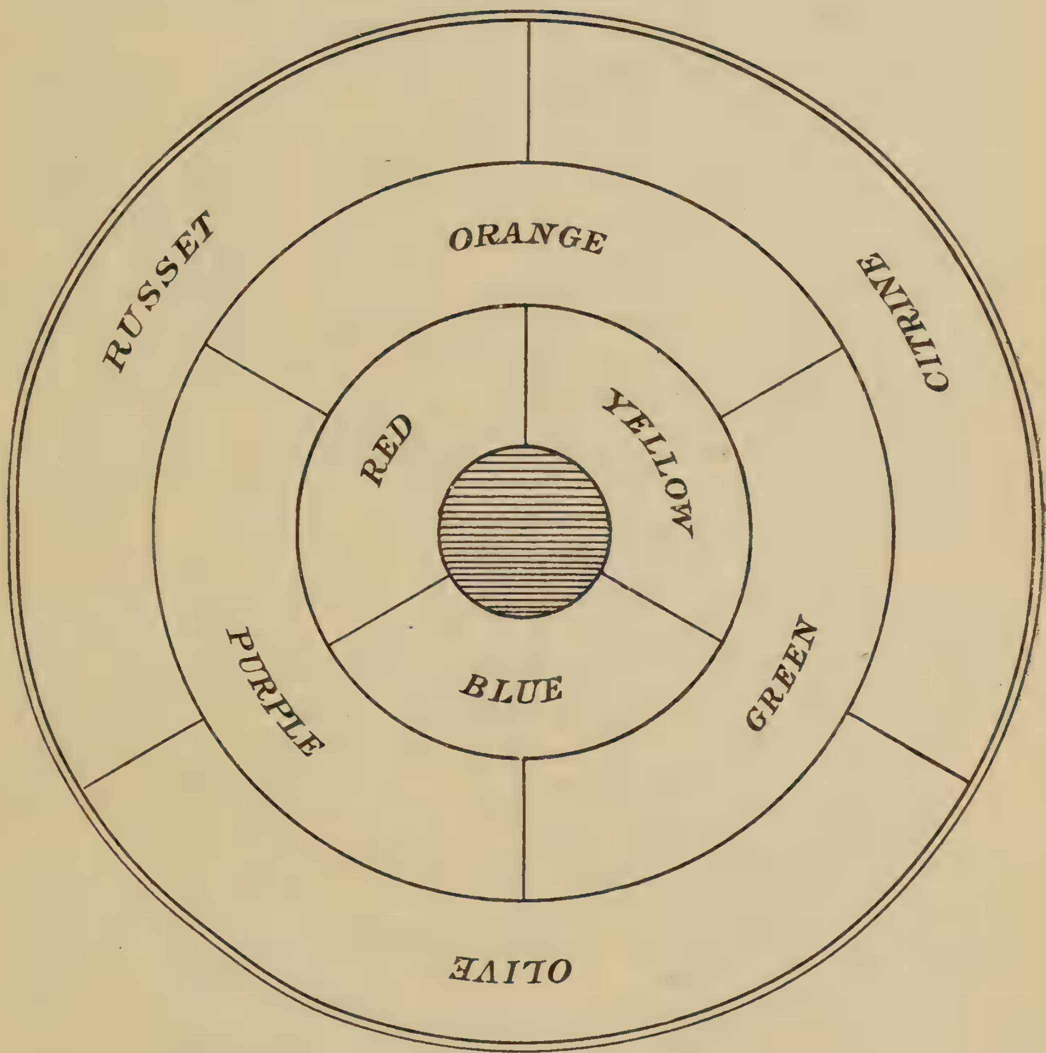

FIG. 62.—Colour diagram.

and upon the use of pigments generally, that all who wish to gain knowledge upon these subjects will have no difficulty in finding instructors.

DIAGRAMS OF COLOUR.—Many diagrams have been published for showing at a glance the so-called primary colours, and their relation to the secondary and tertiary tints, but the most simple is a very old one which we here reproduce (Fig. 62), and in doing

so we must express our regret that we cannot discover the name of its originator. It is extremely useful in at once fixing upon the mind the nature of colour relation so far as pigments are concerned.

The central disc is black, which represents a mixture of the three primary colours—surrounding the disc we find the primaries, yellow, red, and blue. In the next concentric ring are the three secondaries, made up of mixtures of the two primary colours which lie against them. Thus orange is a mixture of red and yellow, green of yellow and blue, and purple of red and blue. Here too we have a ready guide to the complementary colours, a mixture of any two of the primaries, constituting the complementary tint to the remaining primary. Thus green, made up of blue and yellow, is complementary to red ; orange to blue and purple to yellow.

In the outermost ring are the tertiary tints made up of mixtures of the secondaries, thus—green and orange form *citrine ;* orange and purple, *russet* ; green and purple, *olive.*

PECULIARITIES OF PIGMENTS.—The worker who has hitherto confined his attention to black printing will find upon dealing with colours that he has difficulties to meet which at first may seem to be insuperable. Each coloured ink appears to have its own peculiarities, and where, with a black ink, it is possible to temper it with various media so as to alter its working qualities, coloured ink cannot in many cases be so modified. A colour can, of course, be altered by the addition of white to lighten it, or black to darken it ; but what we mean is, that where delicate coloration is necessary, the wholesale addition of turpentine, oil, varnish, etc., is not permissible. Inks of various colours which need no such additions can now be purchased.

PERMANENCE OF PIGMENTS.—Up to recent times the colours employed in the manufacture of printing inks were, with a few exceptions, of mineral origin, and such colours as a general rule are permanent in their nature. And permanence is one of the principal considerations in the selection of a colour, unless the ink is intended for work of quite an ephemeral character.

Aniline Colours.—When the aniline colours first became available in the arts, printers, like many others, were attracted by the gorgeous tints presented by them. The new dyes were quickly made into inks, and bizarre posters with colour schemes never before dreamt of even by those afflicted with acute chromatic aberration appeared on the street hoardings. But only for a brief time, for sunlight mercifully bleached out several of the colours before the prints were many hours old. Any one can test for himself the fugitive nature of many of these aniline colours by exposing any surface

coloured with one of them under a negative in an ordinary photographic printing frame.

More recent work upon the subject, however, has proved that many artificial dye-stuffs are quite as " fast " to light as natural pigments, and that the use of unsuitable dyes by printers and others has been the cause of the general condemnation of the whole class.

Thus *Valenta* * made comparative tests with a large number of aniline colours, taking the alumina oil lake of Alizarine (Turkey Red) as the standard, and found that many of the new lakes were even faster than this.

Among the dye-stuffs included in his report were the following :—

Reds.—Helio Fast Red R.L. and Helio Fast Pink R.L. (By) were much superior to Alizarine ; and Alizarine Red 1B Paste Extra (M.L.B.) was quite equal to the standard.

Yellows.—Helio Fast Yellows 6 G.L. and G.L. (By) were faster than the standard.

Blue.—Helio Fast Blue (By) was very stable and when mixed with the two yellows mentioned, gave a very fast green.

Violets.—Helio Fast Violet (By), Alizarine Direct Violet (M.L.B.) and the Orthocyanines (Berlin) were all exceedingly fast.

Green.—In addition to the green mentioned above, a fast colour was obtained by treating Brilliant Green (which is a fugitive colour) with " green earth " and separating the precipitate.

Experiments on similar lines were made by *Krais* † with coal-tar colours, which were exposed to light for five successive periods of 18, 18, 38, 37, and 221 days respectively under comparable conditions. The pigments were used in the form of water colours, and those not considerably affected at the end of the third period were regarded as suitable for interior work.

Out of 63 colours tested, about 40 were classed as good, and 11 of these were as fast as good mineral pigments, such as chrome yellow, etc.

In the following list these are printed in italics :—

Class A (fast to light even when mixed with a chemically active white pigment). Hansa Yellow 5G, G and R, Helindone Red 3B, Helio Fast Yellow *6GL*, *GL* and RL, *Helio Chrome Yellow GL*, *Algol Red 5G*, *Helio Fast Rose RL*, Brilliant Alizarine Bordeaux R, *Algol Blue 3R*, Alumina Lake from Helio Fast Blue BL, Helio Fast Red 2 GL, Sirius Yellow G, Lithol Fast Yellow GG Extra and R, *Lithol Fast Orange R*, Lithol Fast Scarlet RN, Eglantine BBP, Indanthrene Olive G, Indanthrene Grey B, *Indanthrene Blue GGSZ*

* *Chem. Zeit.*, 1909, xxxiii., 1165.

† *Zeitsch. angew. Chem.*, 1912, xxv., 2193.

and *RZ*, Alizarine Lake from brand V1 extra, Alizarine Iron Lake from brand V2 bluish, Indanthrene Violet RR extra, *Permanent Red 2G extra*, 6B, and 6B extra.

Class B (only fast as pure pigments). Pigment Chrome Yellow L, Alizarine 1B extra 12 per cent., Helindone Violet R, Helio Fast Red RL, Alizarine Red 1B extra, Tuscaline Orange GN, and Green PLX.

In a further series of experiments *Krais** extended the investigation to pigments mixed with oil and exposed on maple wood under glass and in the open air.

As a rule, the results obtained under these different conditions were in most cases in agreement, although there were some curious exceptions.

Contrary to expectation, Alizarine Lake was much faster than a lake from natural madder.

Of the coal-tar dyes examined about twenty were considered to equal the fastest mineral pigments in their permanence on exposure to light.

These included the following :—Helio Fast Red RL, Helio Fast Yellow GL, Algol Red, Alizarine Red, Helio Fast Rose RL, Brilliant Alizarine Bordeaux R, Lithol Orange R, Lithol Fast Scarlet RN, Indanthrene Blues GGSZ, and RZ, Indanthrene Yellow R (BASF), Permanent Red 6B and 4R (AGFA), Pigment Red B (Lake 4 : 100), Hansa Red (Lake 4 : 100), Hansa Yellow 5G (Lakes 4 and 8 : 100), Hansa Yellow R and Alizarine VII Extra, pure 20 per cent. (MLB).

METHODS OF TESTING PERMANENCE.—The only absolutely satisfactory means of testing the fastness of pigments in inks is to expose them to light and air under conditions similar to those they will encounter in practice. For this purpose *Osborn's* colour microscope (p. 179) would be serviceable for keeping a record of the original colour.

In certain cases, however, it is possible to judge of the comparative stability of two colours by exposing them to the action of oxidising agents, as suggested by *Bancroft, Elsenbast* and *Grant* † in the following experiments :—

Chemical Tests.—It was found that certain dye-stuffs were bleached by hydrogen peroxide solution at the ordinary temperature, and by taking the times required for fading as a measure of permanence the dyes examined could be arranged in the following order of fastness, the last being the most fugitive :—Methylene Blue, Azo Red, Methyl Violet, Eosine, Victoria Green, and Magenta.

* *Ibid.*, 1913, xxvi., 74.

† *Eighth Int. Congr. Appl. Chem.*, New York, 1912, Orig. Comm. (Sect. IX.), xx., 91.

The speed of decolorisation varied at different stages of the process, some of the dyes being bleached more rapidly at first and others more rapidly in the later stages, so that over an interval of shorter time the order of stability was somewhat different.

Similar results were obtained when potassium persulphate was used as the oxidising agent.

Solutions of these dyes were also bleached by sunlight and by the rays of a mercury vapour lamp. In the bleaching caused by light the oxidation followed a different course and the dyes could be arranged in the following order of permanency :—Victoria Green, Magenta and Azo Red, Methyl Violet, Methylene Blue, Eosine.

Gebhardt * has pointed out that the fading of dye-stuffs by oxidation in the light is a different process from purely chemical oxidation, the latter being caused by atomic oxygen, and the former by molecular oxygen. This is illustrated by the difference in the behaviour of Methylene Blue, which is faster than Methylene Green (its nitro derivative) against the action of oxidising agents in the dark, whereas when the oxidation takes place in the light Methylene Blue is the more fugitive.

EXPOSURE TO LIGHT AND AIR.—The experiments of *Church* † on the stability of different oil plants exposed to the action of light and air under similar conditions for periods of two or five years are very instructive, and supplement the experiments of *Abney* and *Russell* on moist water colours.

The following were some of the most important results obtained, the depth of the initial colour in each case being represented by 10 :—

Naples yellow,	10·0	No change.
Madder red,	10·0	,,
Madder carmine,	9·5	,,
Madder brown,	9·0	,,
Artificial ultramarine,	10·0	,,
Prussian blue,	8·5	Slightly greener.
Indigo,	8·0	,,
Indian yellow,	8·0	Slightly brown.
Yellow ochre,	10·0	Browner.
Crimson lake,	1·0	Almost gone.
Aureolin,	9·0	No change.

As coloured printing inks are essentially a kind of oil paint, it is not unjustifiable to assume that closely similar results would have been obtained with the same pigments incorporated with lithographic varnish.

* *Zeitsch. angew. Chem.*, 1913, xxvi., 79.
† *Chemistry of Paints*, p. 346.

*Rohland** has found that pigments prepared by the adsorption of dye-stuffs by clays (including kaolin) and talc are faster to light than the original colours. Talc pigments are inferior in covering power to clay and kaolin pigments.

FUGITIVE COLOURS.—Want of permanence is thus a fault which is to be attributed to other colours besides those derived from aniline; and those who would seek information upon this point cannot do better than consult Professor *Church's* book, where a table is given in which pigments are divided into three groups: Class I., containing the truly permanent colours; Class II., those which are subject to a certain amount of change, but which may be used; and Class III., comprising those which ought to be definitely excluded from use.

Following the order adopted in the table referred to, we will now briefly consider the various pigments which are of interest to the printer and manufacturer of printing inks.

WHITE PIGMENTS.—The white pigments named in Professor *Church's* list are three in number, *baryta white*, *zinc white*, and *flake white*. The first named is not used in the making of ink, but it is of secondary interest to the printer in that this description of white is much used in the preparation of surface paper, which is now so much in demand for the effective printing of half-tone process blocks. *Zinc white*, or *zinc oxide*, is much in request by the water-colour artist on account of its permanence; but from some points of view it is not so satisfactory for printing purposes as *white lead* or *flake white*. All these three pigments appear in Church's list as first-class pigments in the matter of permanence, if used for oil painting. But when the particles of lead carbonate are not wrapped up in oil—*i.e.*, when used for water-colour painting, the pigment is rapidly attacked by any sulphurous contamination in the air, and quickly blackens.

New white pigments are *titanium oxide* and *titanium white* (a mixture of titanium oxide and barium sulphate), which have been found very durable for paints owing to the resistance which they offer to the action of light and chemical agents.† Similar advantages are claimed for *antimony oxide*, which is now manufactured in Australia. Like the titanium pigments it gives good results when mixed with zinc oxide.

White printing inks are not much used for ordinary printing except for lightening the colours of other inks. Their chief use is for printing the groundwork of tin plates, boxes, etc., and for this purpose it is

* *Farbenzeit.*, 1912, xviii., 522.

† N. Heaton, *Journ. Soc. Chem. Ind.*, 1922, xli., 216 R.

essential that they shall have good covering-power, be stable in the air, and resist the heat of stoving. Hence zinc white is preferable to white lead for this purpose.

The relative opacities of specimens of white pigments and substrata are given in the table on p. 245.

YELLOW PIGMENTS.—Of yellow pigments there is a very great variety, and although printing in yellow ink is not by itself often called for, except perhaps in poster work, the admixture of yellow with other colours in the formation of secondary and tertiary tints gives it an importance which it might not otherwise possess. We must remember, too, that in three-colour work yellow is one of the three primary tints upon which that process depends for its efficiency.

The most important of all the yellows to the printer is *lead chromate*, usually known as *chrome yellow*. By mixing the neutral chromate with lead oxide yellows of various tones, including the orange, may be obtained, and a mixture of lead chromate and sulphate is employed in the production of certain tints. The so-called canary yellows are made by treating the bichromate solution with citric or tartaric acid, together with sodium sulphate. Here again we have a series of pigments which, while unstable when employed as water colours, are comparatively safe when locked up in oil or varnish, as in the manufacture of inks, although even under these conditions gradual browning occurs on exposure to light. According to *Underwood* and *Sullivan* * chrome yellow made with excess of lead sulphate and in a very cold solution resists the action of light better than any other form of the pigment. Chrome yellow, combined with Prussian blue and with black, gives a great variety of greens (*vide* p. 242). *Vanadium yellow*, *king's yellow* (*orpiment*), *alizarine yellow*, and *alizarine orange* are all liable to change, and the same may be said of *yellow lake*, *brown pink*, *yellow madder*, and *Italian pink*. *Cadmium yellow* and *cadmium orange* may be placed among the permanent colours, but they are too expensive for common use. Of all these yellows, *chrome yellow* is to be preferred on account of its ease in working and freedom from grittiness.

Yellow ochre, *Roman ochre*, and other earths are durable pigments, and are of use to the printer when bright yellow tones are not required. They are also useful for admixture with Prussian blue and other pigments for the production of composite colours. *Raw sienna* and *burnt sienna* come under the same category, the first being a yellow and the second a brownish-red. These last named pigments are extremely hard and require careful grinding.

* *Chemistry and Technology of Printing Inks*, p. 45.

Zinc yellow is fairly permanent, and the same may be said of *Indian Yellow* and *Naphthol. Naples Yellow* (lead antimonate) was found by *Täuber* * to be quite fast to light, but it has the drawback of reacting with iron pigments, such as Prussian blue, and with vermilion.

According to *Täuber, Indanthrene lakes* are satisfactory substitutes for Indian yellow lakes.

RED PIGMENTS.—There are many red pigments which can be used in the preparation of printing inks. *Vermilion*, which is found in the form of *cinnabar* (mercuric sulphide) in many parts of the world, or can be prepared artificially, is tempting because of its beautiful scarlet colour. But ink prepared from it cannot be employed with lead type, for that metal decomposes the mineral and changes its colour. Otherwise there is no reason to suspect the permanence of vermilion when associated with oil or varnish, and *Church* places it among the first-class pigments.

Since vermilion is a very heavy pigment it has a tendency to flake off from the printed impression. This is remedied by the addition of a larger proportion of varnish.

Vermilion, prepared from native cinnabar, was used in the decoration of the walls of Pompeii, wax being the medium with which it was associated. The colour has not faded, although nearly twenty centuries have gone by since the doomed city was overwhelmed by the ashes from Vesuvius. We must, of course, take into consideration the fact that light has been excluded. The Chinese cinnabar is so pure in quality that it merely requires grinding to convert it into the well-known scarlet pigment. Vermilion of first-rate quality is expensive, and cannot come into common use as an ink.

Various substitutes for vermilion have been put upon the market. One of these is obtained by the interaction of lead carbonate and potassium bichromate. Others consist of a basic pigment such as barytes, impregnated with a solution of a coal-tar dye-stuff. None of these cheap products is in any respect equal to vermilion.

Madder.—One of the most valued reds has always been that derived from the madder plant—*Rubia tinctorum* of Linnæus—and until comparatively recent times large tracts of land in India, as well as in the Levant, Holland, and France, were devoted to its cultivation, chiefly for dyeing purposes. But owing to the synthetical production of its chief constituents, *alizarine* and *purpurine*, from anthracene, the cultivation of the madder plant may now be regarded as a discarded industry. Anthracene is derived from

* *Farbenzeit.*, 1910, 1330, 1382.

coal-tar, and the colouring matters which it affords are apparently identical with those formerly obtained from the madder plant. A great variety of different reds, such as *madder carmine*, *rose madder*, *pink madder*, *brown and purple madder*, are obtained from alizarine and purpurine. The best qualities are fairly permanent, but some of the tints are liable to change their tones. The madders come under Class II. in Professor *Church's* list.

Cadmium red is quite fast to light, but is expensive.

In many cases it is possible to replace the madders by coal-tar dye-stuffs, such as *Permanent Red 2G Extra*, *Indanthrene Bordeaux* and *Pigment Scarlet* 3B (see also p. 235).

Carmine.—Carmine, a very unstable compound prepared from the cochineal insect, is sometimes employed to give a fictitious brilliancy to dull reds, but it is so much more expensive than alizarine that it does not now often come under the notice of the ink manufacturers.

Iron Oxide, *Indian Red*, *Turkey Red*, *Persian Red*, seem to be different names for the same thing, ferric oxide, or iron rust. Although not suitable for fine work when used by itself, it is valuable for mixtures with other pigments. Light red and Venetian red are pigments of similar tint, and are varieties of red ochres.

Red lead is a stable colour when used alone, but blends unsatisfactorily with other pigments.

Aluminium Red.—A pigment termed *aluminium red* is claimed by *Allegre* (Fr. Pat. 455,764, 1912), as a valuable substitute for red lead and iron oxide. Its average composition is : Alumina, 52 ; iron oxide, 30 ; silica, 3 ; titanic acid, etc., 3 ; and loss on ignition, 12 per cent. By treatment with hydrochloric acid and potassium ferrocyanide it yields a range of pigments from green to blue, instead of the original red-brown. It is stated to be permanent under atmospheric influences.

BLUE PIGMENTS.—*Ultramarine* is perhaps the most beautiful of the blue pigments, whether it be natural—*i.e.*, made from *lapis lazuli*, or artificial. The artificial ultramarine, one of the cheapest colours, is alone likely to come under the notice of the printer. It is made by calcining a mixture of aluminium silicate, sodium carbonate, sodium sulphate, and charcoal in suitable proportions and grinding the product. Ink made from it is unsatisfactory. It will not work well, and the impressions, even under the hand of a skilled man, are uneven and rough in appearance.

It has also the drawback of reacting with white lead, owing to its containing a certain amount of free sulphur.

Prussian Blue, on the other hand, has many good qualities to

recommend it, and it makes a variety of useful tints when mixed with other pigments. It is transparent, and has great tinctorial power, but when much diluted, or made into a light tint by admixture of a white pigment, is seen to have a greenish hue. Ink made from Prussian blue is generally regarded as being permanent, but it is liable to become pale when exposed to alkaline fumes, such as ammonia. For this reason Prussian blue inks should not be employed in the printing of labels for soap or other substances of an alkaline character. It is not equal in permanence to ultramarine.

Chinese blue is a lighter variety of Prussian blue with a greenish shade, and *bronze blue* is another variety, which shows a metallic lustre when dry.

Cobalt is a permanent blue, but is seldom used by the printer ; and the same may be said of *indigo*, an unstable colour, but one which, with certain yellows, affords useful greens.

Cobalt Violet is remarkably stable but expensive. According to *Täuber* (*loc. cit.*) the lakes of *Alizarine Blue* and *Indanthrene S.*, which are somewhat bluer in tint, are equally permanent.

Indanthrene Blue G. was exposed for eighteen months to the air in water and oil medium, and was found to be quite as fast as cobalt blue, though it was not quite so brilliant as the latter.

GREEN PIGMENTS.—Green pigments for use in the printing press are generally compounded of *Prussian blue* and *chrome yellow*, both of which pigments have already been considered, but in some cases *zinc yellow* (zinc chromate) is used as the yellow constituent of these green pigments, which are termed *chrome greens*. *Chromium oxide*, a remarkably stable compound, is also occasionally used for very fine printing, such as that of bank notes. It is remarkably stable, but is expensive, and has only one hue.

Many greens, like *Emerald green*, *Scheele's green*, *Paris green*, etc., are combinations of copper and arsenic, which are highly poisonous. The first-named possesses a tint of great beauty, which cannot be equalled by any combined pigments, but it is such a very bad working colour that it is not made up as a printing ink. It has, however, sometimes been dusted on to a printed varnish in the same way that bronze powder is attached to such varnish ; but, obviously, the practice is dangerous and should be prohibited.

Cobalt green and *Green earth* are both stable pigments, while mixtures of *Indanthrene yellow* and *Indanthrene Blue* give greens that are quite satisfactory for printing inks.

PURPLE AND ORANGE PIGMENTS.—The others econdary colours, orange and purple, are generally compounded from the

primaries, and an endless variety of different tones is procurable by using the constituents in varied proportions.

Chrome yellow orange is made by mixing the normal and basic lead chromates.

Orange mineral is made by heating white lead in a furnace and mixing the lead oxide with a suitable proportion of lead peroxide to form the compound Pb_3O_4. It has a tendency to form a lead soap with the oil of the ink, which thus becomes what printers term " livery."

BROWN PIGMENTS.—Under the head of brown pigments come a number of earths which owe their coloration principally to *iron oxide*, such as *ochre*, *umber*, *vandyke brown*, *Indian red*, etc. These earth colours are permanent, and are useful in compounding the coarser kinds of printing inks. But it should be noted that for the printing of delicate half-tone blocks such natural colours are quite unsuitable. They always retain their gritty character, even after the most thorough grinding, and this has a very prejudicial effect upon the blocks, which under such treatment soon show signs of wear and tear.

Asphaltum and *Gussow Brown* are sometimes used, but both are fugitive colours.

" **ART SHADES.**"—For such work browns of far richer tone and finer substance may be made by mixing alizarine and other reds with black, to which may be added chrome yellow, Prussian blue, and other colours. So-called " art shades " in printing inks, made up of secondary and tertiary colours with a certain admixture of black to sadden the general tone, are now much in vogue. If the component colours are carefully selected, a half-tone block printed in one of these inks, provided that it has plenty of contrast between full shadow and light tint, appears as if produced by two printings. Such inks have been described for this reason as *double-tone inks*.

It may be mentioned here that such colours as *ochre*, *umber*, etc., which are rich in oxygen, do not require the addition of any separate drying medium when used in the manufacture of printing ink.

ORGANIC LAKES.—Reference has already been made to the use of organic dye-stuffs precipitated on a suitable base to form a lake. These can be obtained in a great variety of tints, and some of those made from diazo dyes will rival any of the mineral pigments in their resistance to the action of light and air (see p. 235).

A full description of the methods of preparing lakes of artificial pigments is given by *Keghel*.* These methods comprise (1) direct precipitation on a substratum, such as kaolin clay, gypsum, barytes,

* *Rev. Chim. Indust.*, Sept. 1920.

lithopone, zinc white, etc. (2) Indirect precipitation on a substratum; (*a*) by means of mineral salts (barium chloride, calcium chloride, lead salts); (*b*) by means of tannin or antimony tartrate. (3) Formation of the pigment on the substratum; (*a*) azo dye-stuffs; (*b*) alizarine dye-stuffs.

Imitations of vermilion, termed "vermillonnettes," are prepared from eosines precipitated on a substratum of red lead with a little lead sulphate or barium sulphate. The finer qualities are precipitated on a base of orange lead chromate and hydrated alumina.

Keghel gives the following typical example of the preparation of a pigment for lithographic work from soluble alizarine dyes:—One kilo. of hydrated alumina is mixed with 30 grms. of alizarine heliotrope R and 5 grms. of turkey red oil, and the mixture boiled for ten minutes with 2 litres of water.

As an example of a lake of an insoluble azo dye-stuff the following formula may be quoted:—Twenty kilos. of Solid Helio Red, R.L., in paste form are mixed with 10 kilos. Solid Helio Red R.L. Extra, and 10 kilos. of a 10 per cent. paste of hydrated alumina. The freshly prepared lake is dull in colour, but, after grinding, is of a fine red colour.

The manufacture of lakes produced by development is based on the diazotisation of an amine, which is then made to combine with a phenol or another amine in a medium containing the substratum. The principal amines used for the purpose are *m*- and *p*-nitro-aniline, the nitro-toluidines, anisidine, nitrophenetidine, benzidine, toluidine, and α- and β-naphthylamines. The pigments of this group have the defect of being more or less soluble in alcohol and in oil.

Basic dye-stuffs are converted into pigments by precipitation with various substances, especially tannin. Many of them yield brilliant lakes when precipitated with a solution of rosin in a lye of caustic soda or sodium carbonate. They are usually precipitated on a substratum together with the resinate of a metal such as zinc or aluminium.

PATENT ANILINE INK.—*Johnson* patented on behalf of the Badische Company (Eng. Pat., No. 12,681, 1903) a method of preparing printing inks from aniline and other organic dyes, which consisted in forming a compound of a colouring matter base with a fatty acid or alkali salt of a fatty acid. For example, a mixture of oleic acid and Benzyl Violet is heated on the water-bath, and the insoluble compound rendered soluble by treatment with caustic alkali. Or sodium ricinoleate is heated with Benzyl Violet or Victoria Green, or sodium ricinosulpholeate with Rhodamine 6G extra.

A violet printing ink may be made by heating a mixture of oleic

acid, Benzyl Violet, potassium hydroxide and printers' varnish ; or by replacing the printers' varnish by printing ink tinted with black an ink of blue tone is obtained.

According to a French patent of *Jagenburg* (No. 399,604, 1909), a solution of a dye-stuff is mixed with a thickening agent such as kaolin, and boiled linseed oil or a resin solution. Barium chloride or a similar salt is then added, and the precipitate collected, freed from water, and ground up with a varnish to form a printing ink.

Tests of Opacity and Covering Power.

Thompson * has published a report on the methods of testing pigments as regards covering power and capacity. Comparisons of opacity should be stated in values referred to a definite volume (not weight) of the pigment distributed in a definite volume of the medium. He defines the coefficient of opacity as the proportion of light, expressed as a fraction of unity, absorbed during transmission through a thickness of 0·01 mm. of the paint, and from this the opacity for other thicknesses. In the case of white paints (and inks) the reflecting power must also be considered.

The apparatus consists of a photometer arranged above two tubes, the lower ends of which are covered with plano-plano-lenses, and below these are two similar lenses. Under these come two total reflection prisms which reflect direct light from a series of incandescent lamps up through the tubes to the eye-piece. The distance between each set of lenses is controlled by micrometer wheels.

A film of the paint is compared with a standard paper, the opacity of which has been photometrically determined, and the test is repeated with a second standard paper. Formulæ for the calculation have been worked out. Results thus obtained with certain pigments were as follows :—

Pigment.	Coefficient of opacity for layer of 0·01 mm.	Reflection.
White lead, Dutch,	0·0671	0·935
White zinc, American process,	0·0794	0·956
White zinc, French process,	0·0645	0·964
Lithopone,	0·0578	0·947
Calcium carbonate,	0·0136	0·969
Basic lead sulphate,	0·0813	0·927
China clay,	0·0190	0·823
Calcium sulphate,	0·0030	0·856
Silica,	0·0102	0·793
Barytes,	0·0114	0·856

* *Journ. Ind. Eng. Chem.*, 1913, v.. 120.

Another apparatus which could be used for this purpose is Pfund's "cryptometer," which measures the covering power of pigments in terms of the number of sq. cm. which 1 grm. of the sample will effectively hide.*

CLASSIFICATION OF COLOURS.—It has long been a practical difficulty common to all commercial crafts that it has not been possible to give in words a description of a particular hue of a colour so that it might be matched by anyone else. It is only necessary to refer to trade catalogues of, say, flowers, textile fabrics, or paints, to see what confusion there is in different minds with regard to the significance of the names of different colours.

In the case of printing inks, the manufacturers work to a more or less accurate standard of colour for their own products, but the printer who orders a coloured ink described by the same name from another manufacturer will probably get a preparation of a totally different tint or hue.

With the object of overcoming this difficulty *Ostwald* † has devised a scheme of classification based on scientific principles, and this system has now been adopted in Germany for the standardisation of colour in all kinds of arts and crafts.

OSTWALD'S CLASSIFICATION OF COLOURS.—In this scheme each colour is classified under a general group heading, and is further differentiated by means of letters and numbers. In the case of the colourless pigments, white, grey, and black, the purest white is represented by the small letter *a*, and the deepest black by *t*, whilst the other letters between represent intermediate stages of grey according to their relative proportions of white and black. In practice, every other stage is omitted, giving the series *a*, *c*, *e*, *g*, *i*, *l*, *n*, *p*, *r*, *t*, which, as a rule, terminates at *p*. These stages are in harmonic relationship with each other, whilst stages apart (*e.g.*, *c*, *i*, *n*) do not harmonise.

The coloured pigments (true colours) are classified into eight main groups ranging from yellow through orange, red, violet, ultramarine, blue, ice blue, sea green, and grass green back to yellow. Each of these groups is subdivided into three grades, so as to give a first, second, and third yellow, orange, red, etc., and the complete circle of colours is divided into 24 standards, differing from each other by about four units. These standards are numbered as follows :—

Colour.	1st.	2nd.	3rd.	Colour.	1st.	2nd.	3rd.
Yellow, .	00	04	08	Ultr. blue,	50	54	58
Orange, .	13	17	21	Ice blue, .	63	67	71
Red, .	25	29	33	Sea green,	75	79	83
Violet, .	38	42	46	Grass green,	88	92	96

* *Bull.* 192, *U.S.A. Dept. Interior Bureau of Mines*, 1922, p. 64.
† *Chem. Zeit.*, 1919, xliii., 681.

In order to indicate the proportion of white and black in a coloured pigment two letters are added from the grey series to the colour number. For example, 17 *l g* indicates a second orange with as much white as in grey *l* and as much black as in grey *g*. The second letter must always be smaller than the first, thus giving 28 derivatives from every colour grade, distinguished by their different proportions of white and black.

With a slight amount of black (*a* or *c*) the colours are transparent or pure, and the opacity rises with the increase in black. With a large content of white (*e.g.*, *c* or *e*) the colours are pale, and they become deeper as the white decreases.

These relationships may be represented by placing all the derivatives of a colour tone in a triangle, the respective angles of which correspond to the pure colour (*v*), white (*w*), and black (*s*), and dividing the triangle into fields by means of lines drawn parallel to the two sides, *v w* and *v s*. These fields number 36, made up of the 28 above-mentioned true colour derivatives and 8 neutral coloured derivatives on the side *w s*. The series in which the colours are here arranged are termed the white equivalents, the black equivalents, and the pure or shade equivalents. The total number of colour standards thus consists of 672 true colours and 8 neutral colours, which are sufficient for most practical needs. *Ostwald*, therefore, urges that these standards should be adhered to, and " wild " colours avoided.

Another method of arranging colours is to keep the letters (*i.e.*, the white and black content) constant and to vary the numbers of the colour tone. In this way 28 equivalent colour circles are obtained, each of which contains 24 colour tones. In these equivalent colour circles there are fundamental harmonies of different colour tones, which may be found by dividing the circles at 2, 3, or more points. In practice nearly all the colours of an equivalent colour circle will give some 250 good combinations, and from these trios and quartettes may be formed.

The law under which neutral colours may be used in harmony with true colours is as follows :—The lightest grey must not contain less black nor the darkest grey less white than the equivalent true colours which form the other constituents of the harmonic whole.

For the purpose of comparison and reference *Ostwald's* colour standards have been recorded in a chart, and an instrument for comparing coloured solutions with them has been devised by *Hahn*.*

THREE-COLOUR PRINTING.

TRICHROMATIC PRINTING.—It is when we come to consider the effect of the introduction of the process block upon colour work that we find changes of the most radical character, not, of course, in the production of mere monochrome impressions, but in the practice of the three-colour, or, as it is often called, the trichromatic method of block printing.

It is not within the scope of this work to consider how far the modern three-colour method of printing will supersede chromo-

* *Zeitsch. angew. Chem.*, 1923, xxxvi., 366.

lithography; probably there will be found an ample field of employment for both processes. But it will be necessary to give a brief outline of the principles which this modern method of producing pictures in colour depends. Like the half-tone process block, the three-colour method of printing is born of the art of photography.

PHOTOGRAPHIC FALSIFICATION OF COLOUR.—It has long been known that the photographic plate gives a very false rendering of coloured objects, blue and violet being represented as white, whilst the warmer tints are shown as black. To understand the underlying cause of this falsification it is necessary to refer to Fig. 63, which represents the solar spectrum in triplicate. In the centre it is shown diagrammatically in the usual manner, with the principal Frauenhofer lines marked by initial letters. Also indicated in this diagram are the prismatic colours, from violet to red. Above the diagram the graduated strip shows how the spectrum appears to the eye, the greatest intensity of the light culminating in the yellow region, and fading away gradually into the red at one end and into the violet at the other end of the scale.

Below the diagram we see a similar graduated strip, representing the solar spectrum as reproduced on the photographic plate, and we are able to note at once that the place of greatest intensity is not near the yellow region, but is far away at the violet end of the spectrum. This is a graphic manner of explaining why upon the photographic picture blue is represented as white, and green, yellow and red as black, or nearly so.

ISOCHROMATIC PLATES.—To *Vogel* is due the discovery that, by associating with the gelatin emulsion which constitutes the surface of a photographic plate certain aniline dyes, its sensitiveness to what we generally call the warmer colours of the spectrum is much increased. These plates are known as isochromatic or orthochromatic, and are used in the camera in conjunction with a coloured screen. The exact position of this screen is unimportant, but a convenient plan is to mount the lens of the camera upon a kind of false front with a slit behind it in which the screen can be inserted.

COLOURED SCREENS.—A simple yellow screen or filter consisting of a glass trough holding coloured liquid, or more conveniently a glass plate coated with coloured gelatin, will, in conjunction with an isochromatic plate, be of service in ordinary landscape work. For example, the brilliant yellow blossoms of gorse in the springtime would be represented as black by an ordinary plate, but with the isochromatic plate and screen they would be almost white. The

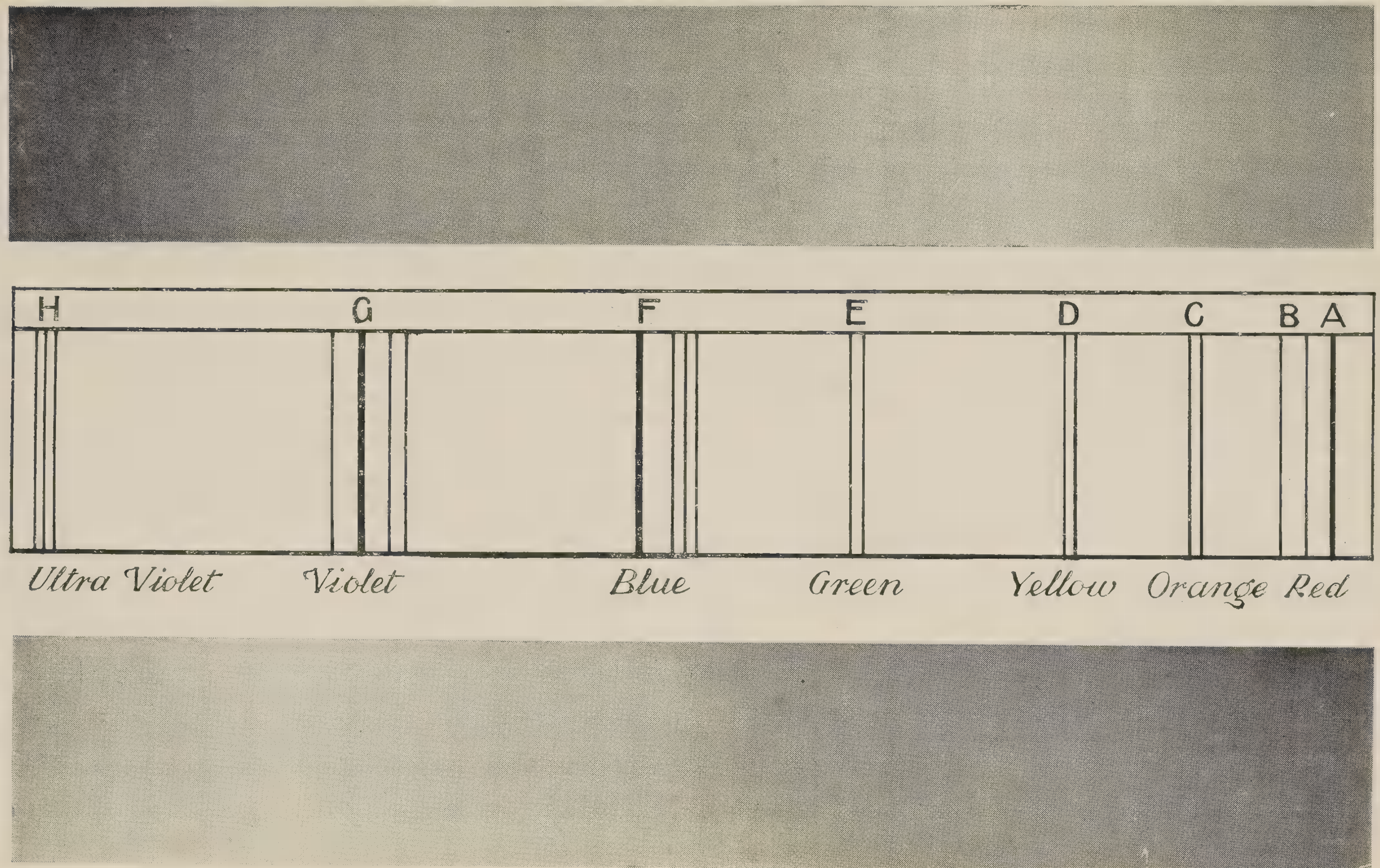

FIG. 63.—SOLAR SPECTRUM IN TRIPLICATE.

foliage tints of autumn can also be now rendered in a manner far more true to nature than was possible before *Vogel's* discovery.

PHOTOGRAPHY AND COLOURED OBJECTS.—But when we come to the representation by photography of oil and water-colour pictures, and different works of art in which colour is an important feature, far more care is necessary in the selection of a proper light filter. The word filter is used advisedly, for the function of the screen is to prevent certain rays passing it, while it gives passage to others. In other words, the required colour is filtered from its associated tints.

CLERK-MAXWELL'S WORK.—The pioneer in this work was *Clerk-Maxwell*, who as long ago as the year 1861 showed in an imperfect manner, for the isochromatic plate had not yet been conceived, that three pictures photographed from one coloured

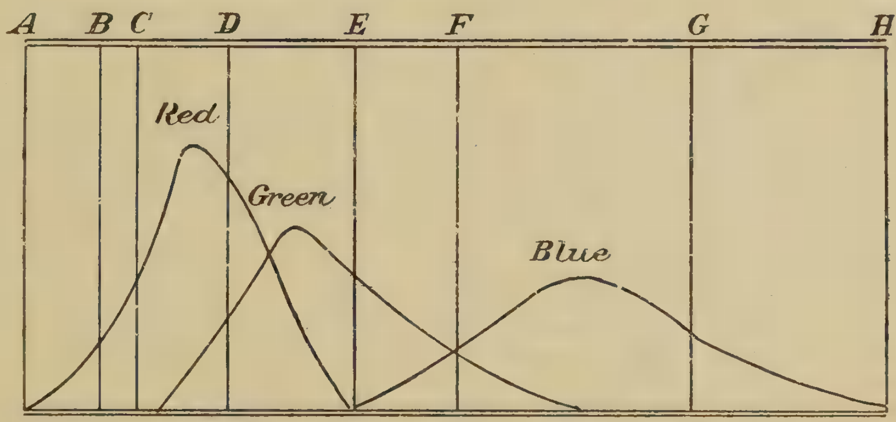

FIG. 64.—Clerk-Maxwell's colour curves.

original but each under a differently coloured screen or filter, would, when combined under suitable coloured lights, amalgamate into a fair representation of the object photographed. *Maxwell's* colour curves have formed the basis of all work in this direction since his time. A representation of these curves is given at Fig. 64. We here see the proportion of the spectrum of which each of the three colour filters should consist, the red taking in a certain part of the yellow and green, the green overlapping the red and blue, while the blue comprises the violet and part of the green.

COLOUR SCREENS OR FILTERS.—By mixing certain aniline dyes, and staining with them glass plates coated with gelatine, screens or light filters can be made to approximate closely in tint to Maxwell's curves. In photographing a coloured object, say an oil painting, three negatives are made, each under its respective

colour filter. From those negatives half-tone blocks are prepared, and it is the printer's business to superpose the images from those blocks in three coloured impressions so as to give a fair representation of the original coloured object.

COLOURED LIGHT.—In dealing with coloured light we find that if we mingle upon a screen the colours red, green and blue from three lanterns, we produce white, or an approach thereto, for white light is composed of all the colours of the spectrum. But if we mix together pigments of the same tones we produce black. In the one case we are working with coloured lights, and in the other with coloured shadows. And when we come to handle pigments such as are employed by painters and in the manufacture of printing ink, we must regard as primary or foundation colours, blue, red, and yellow.

PURE PIGMENTS UNKNOWN.—There is unfortunately no such thing as an absolutely pure pigment, and we can never hope really to match the rainbow colours of the prism; otherwise it would be possible to follow with some accuracy the guide afforded by Maxwell's curves. The ideal pigments for printing in three colours have yet to be found; and ink makers are so alive to the importance of the subject that they are devoting much attention to the production of inks which shall, as far as possible, come up to the scientific standard.

GENERAL CONSIDERATIONS.—The difficulty with which printers have hitherto had to deal is that the ink makers have not worked hand in hand with the makers of light filters to reach one common goal. The colours of screens and of the inks to be associated with them should be fixed and unalterable. Many workers have been in favour of producing the three inks in the first place, taking care that the pigments are as pure in tone as it is possible to procure them, and then of adapting the colour screens or filters to the pigments so chosen. At present there seems to be much confusion reigning, owing to so many workers acting independently of one another; and it thus comes about that A.'s blocks will give results with inks made by C., which are not possible if B.'s inks are used. That this confusion is quite unnecessary must be apparent when we remember that the exact colours of the inks and screens are based upon scientific principles.

EXAMINATION OF TRICHROMATIC PRINTS.—Lastly, we may note that those who would get a fair idea of the way in which separate process blocks can be made by three printings to give all the varied tints of a polychromatic original object, will learn far more by five minutes' careful examination of a good specimen of three-colour printing than they can from many pages of description.

To examine the print a good magnifying glass is needed, for it is necessary to separate the dots of which the picture is composed, and to note their colour and relation to one another.

THE HALF-TONE DOT.—As in all half-tone blocks, these dots are large and crowded together in the shadows, and comparatively small and widely separated in the lights. In the deepest shadows of all, the dots, yellow, red, and blue, are superposed one on the other to form a near approach to black. In other places we find two dots of different colours printed above one another, and giving just the same effect as the same two colours mingled on a palette. In other places we find dots of different colours placed in juxtaposition so that the eye mixes them into a compound tint.

NECESSITY FOR TRANSPARENT INKS.—Now it is obvious that one of the first requisites of the inks used for these built-up tones is that they should possess transparency. An opaque colour, like *vermilion* or *ultramarine*, would at once blot out anything already printed beneath it. We can, therefore, say at once that such colours are inadmissible for this class of work.

OPACITY OF YELLOW PIGMENTS.—The yellow must be of a sulphur hue, and it is not easy to hit upon exactly the right pigment. A transparent yellow which is suitable is not at present to be found, but the difficulty of opacity is partly overcome by printing the yellow block first. Next in order comes red, and there is nothing better than the madder lake which is produced from alizarine. We have already seen that its permanence is good, and it is a very transparent colour. For blue we must use Prussian blue, and as far as possible, the three colours must be so compounded that they possess equal covering power.

SUPPLEMENTARY KEY BLOCK.—Some workers have advocated the use of a supplementary key block printed in black or brown in addition to the usual trichromatic blocks. But this can only be necessary when the original screens, or the coloured inks, are at fault, or when the screens do not represent truly the complementaries of the colours used. If the right colours are employed the superposition of the three inks should produce black, and different shades of grey should be possible by varying the proportions of each. The key block is regarded by the foremost workers as a superfluity.

Gold, Silver, and Bronze Inks.

In printing characters in gold, silver or bronze an ink of a certain degree of viscosity must be used, and the metal subsequently applied either in the form of leaf or of fine powder.

It is preferable that the ink used should be of a colour that will form a suitable groundwork for the metal (for example, burnt umber for use with bronze), and that it is essential that it shall not contain any constituent (such as a pigment containing free sulphur) that will react with the metal.

Seymour * recommends a varnish prepared by incorporating melted beeswax with lithographic varnish to form a paste-like medium.

"Dutch-leaf," an alloy of copper and zinc, is extensively used in the preparation of metallic powders for the printer, and the colour is varied by altering the composition of the ingredients.

Inks for Cheques and Bank Notes.

Under the head of "Printing inks that change colour on the application of an acid," *Savage* † tells us of a black ink, the method of making which was for a long time kept a profound secret "by one house in the city of London," which was designed to prevent fraudulent alterations in bankers' cheques, etc. And he suggests that, in addition to this precaution, the whole paper of such documents should be covered with a delicate lace pattern in a light-coloured ink, so that should any attempt be made to remove writing upon such a draft by means of acid, the pattern and the printed words would disappear as well as the writing ink. The black ink, for which he furnishes a recipe, is made of galls, iron, and logwood, and is precipitated, dried, and ground with soap, turpentine, and balsam of capivi.

For the purpose of printing the lace-like pattern over the surface of the paper he recommends the lake of commerce, ground up with varnish and a large proportion of curd soap. This ink he actually tried, and found that it would not resist oxalic acid, but he states that any colour of vegetable origin might be adapted to the same purpose. He expresses the hope that, from the hints which he has given, the subject will be pursued and the method made perfect—and asserts that if he should thus prove to be the means of preventing the commission of crime, it would be a source of the highest gratification.

In the earliest attempts to guard against fraud by alterations in cheques, etc., attention was directed to the writing ink to be used, and numerous so-called "safety inks" (p. 280) were devised.

* *Modern Printing Inks*, p. 73.

† *The Preparation of Printing Ink*, 1832.

Obviously, however, such inks would only be used to a limited extent, and the necessity for them has been obviated to a considerable extent by the introduction of various methods of printing the groundwork of the cheque with special inks that would permanently change colour on the addition of any of the usual reagents employed to remove ordinary iron gall inks.

PATENT INKS FOR CHEQUES, ETC.—A process patented by *Seropyan* (Eng. Pat., No. 1,744, 1857) was devised to prevent the counterfeiting of bankers' drafts and other documents by photography. Two or more colours were used, each of which "absorbed light." The groundwork of the note was printed in one of these (*e.g.*, yellow, red, or orange), whilst the other was made into an ink for printing the design and figures on the note, and was as fugitive as the ground colour. An ink of this type consisted of iron hydroxide and gallic acid ground in boiled linseed oil. Documents thus printed gave only a blurred photographic copy, whilst any attempts to remove the ground colour simultaneously removed the design. *Vogel's* discovery of colour sensitive plates destroys whatever value there was in this invention.

In *Moss's patent* (Eng. Pat., No. 348, 1859) the paper pulp for the notes was incorporated with a pigment, such as chromium oxide or burnt clay; whilst an ink for printing the notes contained burnt China or other clay and sulphur, with or without a pigment. It was stated that any attempt to remove the colour or printing would render the note useless for circulation.

A permanent printing ink for bank notes invented by *Edson* (Eng. Pat., No. 3204, 1863) consisted of a compound of stannic oxide with chromium oxide or other metallic oxide.

In 1876 *Pinkney* (Eng. Pat., No. 4470) claimed a process of treating the note with a substance that would form an insoluble compound with ordinary writing ink, and mentioned in particular soluble non-deliquescent ferro- and ferri-cyanides with an aniline or vegetable colour as suitable for the purpose.

In *Nesbit's* patent (No. 4204, 1879) ordinary lithographic ink was dried, powdered, and mixed with an aniline dye-stuff soluble in water, the whole being mixed with turpentine or other liquid which would not dissolve the aniline dye-stuff. Cheques printed with this ink would be smeared on applying any aqueous reagent to remove writing.

A special method of preparing paper for cheques by immersion in copper sulphate and ammonium carbonate solution, and subsequently in an alkaline solution of cochineal with alum and glycerin, was provisionally protected by *Haddan* (Eng. Pat., No. 4997,

1879). This paper would change colour on contact with the reagents used to remove writing ink.

A process with the same end in view was patented by *Dupré* and *Hehner* (Eng. Pat., No. 375, 1881). The preparation used for printing the note consisted of a sulphide insoluble in water, but acted on by dilute acids (*e.g.*, zinc sulphide), with lead carbonate or other salt of a heavy metal. The mixture was worked into a paste with glycerin, treacle, and gum arabic, and could be used for printing invisible characters on the cheque, or added to the coloured paste for printing the groundwork. On applying acid, alkali, or cyanide to a cheque thus treated, dark stains would be produced immediately.

A method of preventing the obliteration of printing ink by means of solvents for oils, and especially the cancelling marks on postage stamps, was devised by *Nesbit* (Eng. Pat., No. 949, 1883). It consisted of the use of a printing ink prepared by incorporating an extract of alkanet root with oil. Any attempts to remove ordinary printing ink would blur the printing done with this ink. In 1896 *Webb* (Eng. Pat., No. 26,992) patented an aniline safety ink for copper and steel-plate printing of cheques and the like.

In a process patented by *Rowan* (Eng. Pat., No. 3909, 1904) the paper is impregnated with potassium ferrocyanide and ammonia, and the printing done with an ink containing ferric chloride, potassium iodide and caustic soda. The oily medium prevents the interaction of the ingredients, but a stain is produced when there has been any tampering with acid or alkali. The addition of magenta or manganese to the ink intensifies the stain.

Analysis of Printing Inks.

In examining a printing ink it is necessary to separate the pigment from the oil medium by means of a suitable solvent. In some cases a mixture of alcohol and ether will be found satisfactory, the insoluble matter being collected upon counterpoised filter papers and weighed.

In *Nicolardot's* * process of analysing paints the sample is treated with hot toluene to separate the oil from the mineral matter; the latter is then decomposed with hydrochloric acid beneath the surface of the toluene, the liberated hydrogen sulphide oxidised by being passed through tubes containing nitric acid and potassium permanganate solution, and the sulphate determined. The residue of oil from the toluene extract is dried at 105° C. and weighed.

* *Ann. Chim. Anal. Appl.*, 1913, xviii., 184.

As filtration of the solution from the finely divided pigment is often difficult owing to the particles blocking the paper, centrifugal force may be used effectively for the separation.

The insoluble residue containing mineral pigments, lamp-blacks, insoluble lakes of dye-stuffs, and filling materials, such as silica, etc., is examined by the usual methods. Any soluble pigment dissolved by the solvent is separated by methods outlined on p. 138, *et seq.*, and its nature determined.

Four commercial printing inks examined by the writer had the following composition :—

1. *Yellow.*—Contained 52·4 per cent. of lead chromate.

2. *Yellow.*—Contained 54·6 per cent. of oil, and 23·07 per cent. of mineral matter, mainly alumina and silica. The pigment gave the reactions of Aurine.

3. *Blue.*—Contained 35·74 per cent. of Prussian blue.

4. *Red.*—Contained 45·66 per cent. of oil, 15·86 per cent. of ash (largely alumina), with an alizarine pigment.

PRACTICAL TESTS.—The behaviour of a printing ink in practice is obviously a matter of much more importance than its exact composition, and it is desirable that a series of practical tests should be applied in the laboratory and the results checked by parallel tests on the machine.

Specifications for the tests to be applied to the inks used in the U.S.A. Government Printing Office have been published.* For example, half-tone black ink must answer to the following requirements :—

1. *Non-Separation of Oil from Pigment.*—The oil or varnish should not separate from the pigment either on the face of the type or cuts, or in the fountain, but should be short enough to break up readily in the distribution and not "string."

2. *Transfer.*—In transferring from type or cuts to paper the ink should leave the face of the type or cuts reasonably clean.

3. *Hardness.*—Ink should dry hard on paper in eight hours to admit of easy handling without damage or injury to the work, and should not pull the coating or the face from the paper, nor the face from the roller.

4. *Drying.*—Ink should not dry on the form, rollers, or distribution so that it may not be easily removed therefrom.

5. *Offset or Smutting.*—The ink must be able to carry sufficient colour to print sharply and cleanly, without offset or smut on sheets falling on top from the press fly or in piling the work.

6. *Colour.*—The ink must dry a deep solid carbon (not aniline) black, and not turn grey, nor have a metallic sheen or lustre, nor blister the paper.

7. *Quantity Required.*—The weight of the amount used must be noted and averaged on a basis of 5,000 printed pages.

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* *The Composition, Properties, and Testing of Printing Inks*, Bureau of Standards, Washington. Circ. No. 53, 1915.

METHODS TO BE USED IN MAKING THE PRACTICAL TESTS.

1. The practical test of half-tone black ink shall be made on the flat-bed presses in use in the Government Printing Office.

2. The test shall be made on coated book paper of the size, weight, and quality in general use in the Government Printing Office.

3. The type or cut forms shall be previously "made ready," and the press otherwise in good condition to make a satisfactory run.

4. The form, rollers, distribution, and ink fountain shall then be thoroughly washed and cleaned. The ink to be tested shall be weighed before being placed in the fountain. The quantity to be tested should be sufficient to run for not less than three hours, and preferably a run of five hours should be made.

5. Ink that will separate the oil or varnish from the pigment on the face of the form or in the fountain will not be accepted.

6. To be satisfactory, ink under the impression should transfer from the face of the type or cuts to the paper, leaving the face of the type or cuts reasonably clean. It should be heavy in body, should feed well, and have sufficient "tack" to dry on the paper rapidly enough while printing to avoid the necessity of using slip sheets; but it should dry hard on the paper in eight hours, so that the work can be handled easily without damage or injury to the printing. It must not pull the face or coating from the paper and leave it on the face or form, or pull the face from the rollers. It should be removed easily from the form, rollers, and distribution, and must be able to carry sufficient colour without offset or smut, and give a clean, sharp impression.

7. See requirement No. 7, *supra*.

After the test has been made, the remaining quantity of the ink shall be removed from the fountain and weighed, a reasonable allowance being made for the ink necessary left in the fountain, on the rollers, and distribution, in order to determine the number of copies a given quantity of ink will print.

DEFINITION OF TERMS.—With the object of obtaining uniformity in the sense in which various terms are used in connection with printing inks, *Underwood* and *Sullivan* * suggest the following definitions :—

Hue.—When two pigments are mixed to produce a new colour and one predominates—*e.g.*, violet-red, blue-green.

Tint.—Pigment lightened with white.

Shade.—Pigment darkened with black or a complementary pigment.

Colour Strength.—Tinting power when mixed with white.

Abrasive Quality.—Presence of hard material.

Livering.—Thickening of ink to a spongy mass, due to chemical action between the pigment and medium.

* *The Chemistry and Technology of Printing Inks*, by N. Underwood and J. V. Sullivan, 1916.

Shortness.—Pigment remaining stiff when mixed with a large amount of oil.

Flow.—Property of pigment to combine with good body to give an ink which will run well on the press.

Length.—Capacity of an ink which flows well to be drawn out into a string.*

Tack.—Degree of cohesion between the particles of an ink; it may be described as the pulling power of the ink against another surface.

Softness.—Absence of tack.

Body.—Density of a pigment.

Bleeding.—Penetration through the paper of certain pigments which are partially soluble in water or in oil.

* According to the U.S.A. Bureau of Standards, Circ. No. 53, an ink varnish is " long " when a drop falls away from a spatula with a long hairy string or thread; it is " short " when the drop is cut off sharply with a very small tail.

SECTION III.

INKS FOR MISCELLANEOUS PURPOSES.

CHAPTER XII.

COPYING INKS.

Contents.—Various copying inks—Patent copying inks—Copying papers—Copying ink pencils—Manifold copying apparatus.

Most writing inks are capable of yielding one or more copies when pressed with a suitable moist paper soon after writing. Thus an ordinary iron gall ink of the old type will give a faint copy before it has become completely oxidised, but when once the pigment has become completely insoluble copies can no longer be taken.

As the process of copying tends to make the original writing too faint, it is necessary to have an additional quantity of pigment in the ink, together with a certain proportion of gum or other adhesive material to attach this excess of colouring matter to the surface of the paper, and to protect it from too rapid oxidation.

In the case of "alizarine" inks the iron tannate becomes insoluble as the writing dries, and although the indigo or aniline dyestuff remains soluble in water, it becomes so enveloped in the resinous tannate (see p. 184) that eventually it does not yield any colour to paper when pressed.

Logwood inks yield reddish-grey copies, which gradually oxidise and become black. When the writing is completely dry only faint copies can be taken.

Dextrin is sometimes employed in place of gum to form a sort of varnish over the writing to prevent early oxidation. Sugar, too, is added for the same purpose, but has the drawback of leaving the writing more or less sticky.

Viedt * considers that many copying inks contain too large a

* *Dingler's polyt. Journ.*, 1875, ccxvii., 148.

proportion of adhesive substance, and is of opinion that from 30 to 50 grms. of gum arabic per litre is quite sufficient for a good ink.

A small amount of glycerin is a common constituent of copying ink, its object being to prevent the gum from completely drying. If, however, it be added in too large an excess the ink will smudge, as is the case with a certain commercial copying ink that contains as much as a third of glycerin.

Even in *Böttger's* copying ink (*infra*) the proportion of glycerin (120 grms. per litre) is too high, and in *Viedt's* opinion only a sixth of this amount is required to make an excellent copying ink on those lines.

Speaking generally, iron gall and logwood inks should contain from 30 to 40 per cent. less water than inks of the same formula intended for use as writing inks only.

VARIOUS COPYING INKS.—Of the numerous published formulæ for copying inks the following are selected as typical, whilst others can easily be calculated by modifying the composition of writing inks given (pp. 110 to 119), in accordance with the general considerations given above :—

*Stark's Patent Copying Ink.**—Logwood extract, 250 grms. ; iron sulphate, 17 grms. ; copper sulphate, 17 grms. ; alum, 100 grms. ; and sugar, 50 grms., in a litre of boiling water. The sodium is subsequently mixed with 16 grms. of potassium chromate, 100 grms. of glycerin, and 200 grms. of sulphindigotic acid.

Böttger's Alum Logwood Copying Ink.†—One part of alum, 2 of copper sulphate, and 4 of logwood extract are boiled with 48 parts of water, and the solution filtered. Copies made with this ink are faint at first, but soon become dark.

A later modification of this ink was made by *Böttger* ‡ in the following manner :—Logwood extract, 30 grms., and crystalline sodium carbonate, 8 grms., are boiled with 250 c.c. of water, and the solution mixed with 30 grms. of glycerin (sp. gr. 1·25), 1 grm. of potassium chromate, 8 grms. of powdered gum arabic, and (preferably) about 1 grm. of copper sulphate to strengthen the colour.

Délidon's Patent French Copying Ink.§—Galls, 10 grms., ferrous sulphate, 100 grms., and logwood, 300 grms., are boiled with $1\frac{1}{2}$ litres of water down to 1 litre. The solution is then mixed with 250 grms. of molasses, 15 grms. of gum, and 50 grms. of alcohol containing 5 grms. of an essential oil as preservative.

* *Dingler's polyt. Journ.*, 1875 , ccxvii., 76. † *Ibid.*, 1859, cli., 431.
‡ *Ibid.*, 1869, cxci., 175. § *Wagner's Jahresber.*, 1873, xix., 842.

*Dieterich's Violet Logwood Ink.**—Logwood extract solution (20 per cent.), 600; sulphuric acid, 0·5; mixed with a solution of aluminium sulphate, 40; oxalic acid, 40; potassium carbonate, 40; potassium bichromate, 4; and phenol, 1; in 250 parts of water. This ink yields excellent copies.

Walther † gives the following directions for the preparation of a logwood copying ink, based on the property of hæmatein to yield copies when oxidised in the presence of aluminium compounds:—Logwood extract (30 kilos.) is dissolved in 100 litres of hot water, and 1·7 kilo. of crude sulphuric acid (sp. gr. 1·84) is added to the solution. In a second vessel a solution of 8 kilos. of aluminium sulphate in 40 litres of water is slowly treated with 6 kilos. of calcined sodium carbonate (= 13·2 kilos. of the crystalline product), and the precipitated aluminium carbonate is dissolved by the gradual addition of 8 kilos. of cyrstalline oxalic acid. A solution of 1 kilo. of potassium bichromate in 20 litres of hot water is prepared in a third vessel, and the three solutions are mixed and boiled for 15 minutes. There should be a gradual change in the colour through red to violet, and when this stage is reached the ink is made up to 210 kilos., with the addition of about 200 grms. of an antiseptic agent, and left for at least 8 days. The colour is regulated by varying the proportion of bichromate and acid. The more acid used, the redder the ink. If necessary, ammonia may be added to reduce the acidity.

Dieterich's Gall Copying Inks.—Dieterich ‡ has prepared copying inks from oxidised gall extract and oxidised tannin solution prepared as described on p. 117.

Black Oxidised Gall Ink.—900 parts of the oxidised gall extract with 4 of sulphuric acid (sp. gr. 1·835) and 60 of ferrous sulphate, decanted after three weeks and diluted to a litre.

Black Oxidised Tannin Ink.—600 parts of oxidised tannin solution mixed with a solution of 60 parts of ferrous sulphate in 350 parts of water, filtered after three weeks and diluted to a litre.

For coloured copying inks, these inks are mixed with various aniline dyes, such as phenol blue, 2·5 parts per litre; 6 of Ponceau red; 6 of aniline green; 1·5 of phenol blue and 2·5 of aniline green (for blue-green); 1·5 of phenol blue and 2·0 of Ponceau red (for violet), etc.

Aniline Copying Inks.—Many of the commercial copying inks are prepared from aniline colours, which, being soluble in water and not readily undergoing oxidation, enable copies to be taken at any subsequent period.

* *Pharm. Manual*, 1897, p. 685. † *Chem. Zeit.*, 1921, xlv., 432.
‡ *Pharm. Manual*, 1897, p. 683.

Dieterich * gives the following formulæ for such aniline copying inks :—

Violet.—20 of methyl violet, 3 B, in 940 of warm water, with 10 of sugar, and 2 of oxalic acid.

Blue.—10 of resorcin blue in 950 of water, with 10 of sugar and 2 of oxalic acid.

Red.—Eosin, 25 ; sugar, 30, in 100 of cold water ; subsequently filtered.

The following dye-stuffs manufactured by the *Badische Company* are suitable for copying inks :—

Violet Inks.—(*a*) *Crystal Violet*, the hydrochloride of hexamethyl-pararosaniline.

(*b*) *Methyl Violet* O and III. extra N, which are of similar chemical composition.

Green Inks.—*Diamond Green*, B and G (*cf.* p. 136).

Red Inks.—*Diamond Magenta* and *Magenta Powder*, which are mixtures of the hydrochloride and acetate of pararosaniline, and the corresponding salts of rosaniline respectively.

Safranine T. *extra*, being phenyl- and tolyl-tolusafranin chlorides.

Black Inks.—A combination of the above violets, greens, and reds with chrysoidine (diamino-azobenzol hydrochloride) yields a black copying ink.

PATENT COPYING INKS.—Numerous British patents have been taken out for the preparation of copying inks and papers, of which the following are the more important. The modern method of copying by means of pressure and a special ink is due to *James Watt*, the engineer (Eng. Pat., No. 1244, 1780), whose copying press was of the same form as in use to-day. The addition of glycerin was first claimed by *Henry* (Eng. Pat., No. 1132, 1858), whilst *Roberts* (Eng. Pat., No. 1213, 1862) added molasses and an extract of *albemosch* seeds, in addition to glycerin. The use of glycerin was also claimed by *Winstone* (Eng. Pat., 1996, 1858), by *Cooke* (Eng. Pat., No. 47, 1869), and by *Coën* (Eng. Pat., No. 3247, 1891). In *Conrad* and *Lilley's* patent (No. 2011, 1890), indigo carmine, aniline black, glycerin and magnesium chloride are added to an ordinary iron gall ink ; whilst the addition of a deliquescent salt, such as ammonium nitrate, with the glycerin is protected by *Conrad* (Eng. Pat., No. 10,401, 1890).

Aniline dye-stuffs enter into the composition of several of the patented inks, that of *Kwayser* and *Hasak* (Eng. Pat., No. 4606,

* *Ibid.*, p. 687.

1878), consisting solely of an aqueous or alcoholic solution of an aniline colour.

Copying inks in the form of a powder were patented by *Byford* (Eng. Pat., No. 974, 1876) and by *Jacobsohn* (Eng. Pat., No. 1586, 1878), the latter being prepared by evaporating to dryness a solution of aniline dye with sugar, gum, etc.

COPYING PAPERS.—One of the earliest methods of chemical copying was that devised by *Underwood*,* in which use was made of the principle of writing with a decoction of logwood as the ink, and moistening the writing with a solution of potassium bichromate before taking the copy. Under these conditions the ink is only formed at the time of writing, and several copies can be made. This method was patented (Eng. Pat., No. 1112, 1857), and was adopted by Government offices and important firms, but, like all the other early processes of copying, it has been to a large extent replaced by the methods of carbon paper and stencil duplication. The special copying paper claimed by *Piffard* (Eng. Pat., No. 10,905, 1890) was prepared by treating paper with a saturated solution of gallic acid, and was used with an iron ink. In *Beales*' patent (No. 17,373, 1890), the paper consists of tissue paper saturated with a solution of loaf sugar and silver nitrate in a mixture of water and glycerin, whilst the ink is an iron gall logwood ink containing glycerin and vegetable black. Both of the above inks are stated not to require a copying press.

Another special copying paper is that protected by *Brown* (Eng. Pat., No. 3807, 1900), which is coated on one side with hardened gelatin, and on the other with a deliquescent salt such as calcium chloride and a solution of a substance not affected by ordinary ink. This paper does not require damping.

Cameron (Eng. Pat., No. 16,515, 1910) claims the use of paper moistened with a solution of tannic or gallic acids to obtain copies from writing in ordinary ink. To prevent smudging sodium sulphate or an alkaline salt is added to the liquid. In the case of logwood inks the copying paper may also contain alum.

COPYING INK PENCILS.—These consist of a base, such as powdered graphite and kaolin clay mixed with a very concentrated solution of methyl violet or other aniline dye-stuff into a paste, which is pressed into sticks and dried. In *Viedt's* † opinion the use of gum arabic as a binding material is less suitable. Provisional protection was claimed by *Petit* (Eng. Pat., No. 4090, 1874) for a copying ink pencil prepared in this way.

The writer has analysed the pigments in copying ink pencils typical of those sold from 1908 to 1918. The dye-stuffs varied from

* *Journ. Soc. Arts*, 1857, 67. † *Dingler's polyt. Journ.*, 1875, ccxvi., 96.

less than 25 per cent. to about 50 per cent., the mineral matter from 2·79 to 56·1 per cent., and the graphite from about 12 to 68 per cent.

The pigments could be classified into four groups—viz., (1) those composed of graphite and dye-stuff only; (2) those in which dye-stuff had been incorporated with approximately equal proportions of kaolin and graphite; (3) those with kaolin largely in excess; and (4) one where the graphite predominated.* The methods of differentiating between these pigments and their properties are dealt with in full elsewhere.†

MANIFOLD COPYING APPARATUS.—The well-known simple apparatus known as a *graph* is composed of a stiff gelatin bed, which receives the impression of the writing and enables several copies to be taken. The ink usually consists of an aqueous solution of methyl violet or other soluble aniline dye with glycerin and gum. This type of copying apparatus was patented by *Rosefeld* in 1879 (Eng. Pat., No. 2256), the block consisting of gelatin, molasses or sugar, acetic acid, and iron oxide, with sodium bisulphite to prevent decomposition of the gelatin. Special aniline and metallic inks for manifold copying apparatus were also patented by *Hardt* (Eng. Pat., No. 4187, 1879).

Another copying apparatus of the same type, protected by *Schmitt* (Eng. Pat., No. 948, 1881), contained glycerin and chrome alum in the jelly, whilst the ink contained a colour, such as indigo and a uranium salt, and had a chemical action on the bed. The impression produced on the bed was capable of receiving printing ink. The drawback of gelatin copying apparatus is that the jelly soon becomes saturated with the aniline ink and is no longer capable of yielding clean copies. This is obviated in the apparatus protected by *Smith* (Eng. Pat., No. 7,149, 1888), which consists of a slab composed of a mixture of china clay, starch, glycerin, and water, from which the impression can be completely removed by means of a sponge after use. The ink in a solution of an aniline colour in a mixture of water, alcohol, and hydrochloric acid.

Desmarest and *Lehner* ‡ give the following proportions for a graph recommended in France by the Minister of Public Works:—Glue, 100; glycerin, 500; natural barytes or washed kaolin, 25; and water, 375 parts. *Keghel* § gives the following formula for a black hectographic ink:—Aniline black (hydra), 8; acid violet 10B, 1; brilliant croceine, 2; glycerin, 10; gum arabic, 1; and water, 100 parts.

* *Analyst*, 1917, xliii., 3.

† *Documents and their Examination*, 1922, p. 118.

‡ *Manuel Pratique de la Fabrication des Encres*, 1923, p. 114.

§ Desmarest and Lehner, *loc. cit.*, p. 119.

CHAPTER XIII.

MARKING INKS.

CONTENTS.—The ink plant of New Granada—The Indian marking nut—The Cashew nut—Rhus toxicodendron—Rhus venenata—Rhus radicans—Other vegetable juices—**Chemical marking inks**—Silver inks—Gold marking inks—Platinum marking inks—Marking inks containing other metals—Aniline marking inks—Indigotin marking inks—Alizarine marking ink—Examination of marking ink—Marking ink pencils.

NATURAL VEGETABLE INKS.

NUMEROUS plants contain a juice, which is oxidised on exposure to the air, yielding black or brown pigments, often of great durability; and such natural inks have been employed in various parts of the world, either for writing or for marking linen.

Jametel,* quoting from ancient Chinese documents, states that prior to about 2697 B.C. the Chinese used a kind of vegetable varnish for ink, and not the product which is now known as Chinese or Indian ink. It is probable that this ink was the juice of a species of *Rhus* (*vide infra*).

THE INK PLANT OF NEW GRANADA.—According to *Johnson*,† the juice of *Coriaria thymifolia*, known locally as *chauci*, or the "ink plant," is at first red, but rapidly changes in colour, becoming deep black in a few hours.

The juice can be used as ink without any treatment, and gives a very stable writing, which is not affected by sea-water. *Johnson* states that all the older documents in Spanish South America were written with this ink.

It is also a native of New Zealand, where too it goes by the name of the "ink plant." ‡

THE INDIAN MARKING NUT.—The fruit of the Indian tree, *Anacardium orientale*, which is now termed *Semecarpus anacardium* (Fig. 66), has long been known as the "marking nut," from the

* *Loc. cit.*, Introd. p. x.

† *Universal Cyclopædia*, New York, 1894, art. *Ink.*

‡ Smith, *Dict. of Economic Plants*, p. 132.

fact that its juice makes a very dark and durable stain on linen or paper.

The tree is found throughout the hotter parts of India, though not in Ceylon, and is also met with in the Western Indies and in Northern Australia. The juice which acts as ink is contained in a series of

FIG. 66.—Indian marking nut (*Semecarpus anacardium*).

cells (see Fig. 67). The ripe fruit is yellow in colour, and is eaten after roasting by the natives. As met with in commerce it is a black oval or heart-shaped substance, about 2 cm. in length, and the same in breadth, and $\frac{1}{2}$ cm. thick. The white kernel is covered by a reddish pellicle.

The natives prepare the ink from the unripe fruit, and use it

when mixed with quicklime for marking cotton and linen, on which it produces a very permanent mark.* The dried juice is also extensively employed in the manufacture of a black varnish.

Lewis † found that the juice required warming to make it flow freely. The writing done with it was first reddish-brown, but rapidly became deep black and was very indelible.

The brown oil from the mesocarp dissolves in potassium hydroxide solution, giving a green solution, whilst the alcoholic solution becomes black on the addition of basic lead acetate.

FIG. 67.—Section of marking nut, showing cells containing the juice.

The juice has a very irritant action upon the skin, producing symptoms similar to eczema, and the same effect is said to be produced by the fumes given off on roasting the nut.

We have made a number of experiments with the dried nuts. The black viscous juice surrounding the kernel of these had a characteristic aromatic odour and produced a light brown stain, which gradually darkened on exposure to the air.

A decoction of the broken nuts in boiling water rendered alkaline

* σῆμειον = a mark, and καρπος = fruit.

† *Philosophico-Technicum*, 1763, p. 329.

with ammonia yielded a dark fluid, and the characters made with this on paper or linen were dark brown, and very resistant to the action of reagents. They were not removed by bromine, oxalic acid, or hydrochloric acid, whilst alkalis rendered them darker. They were soluble, however, in ether.

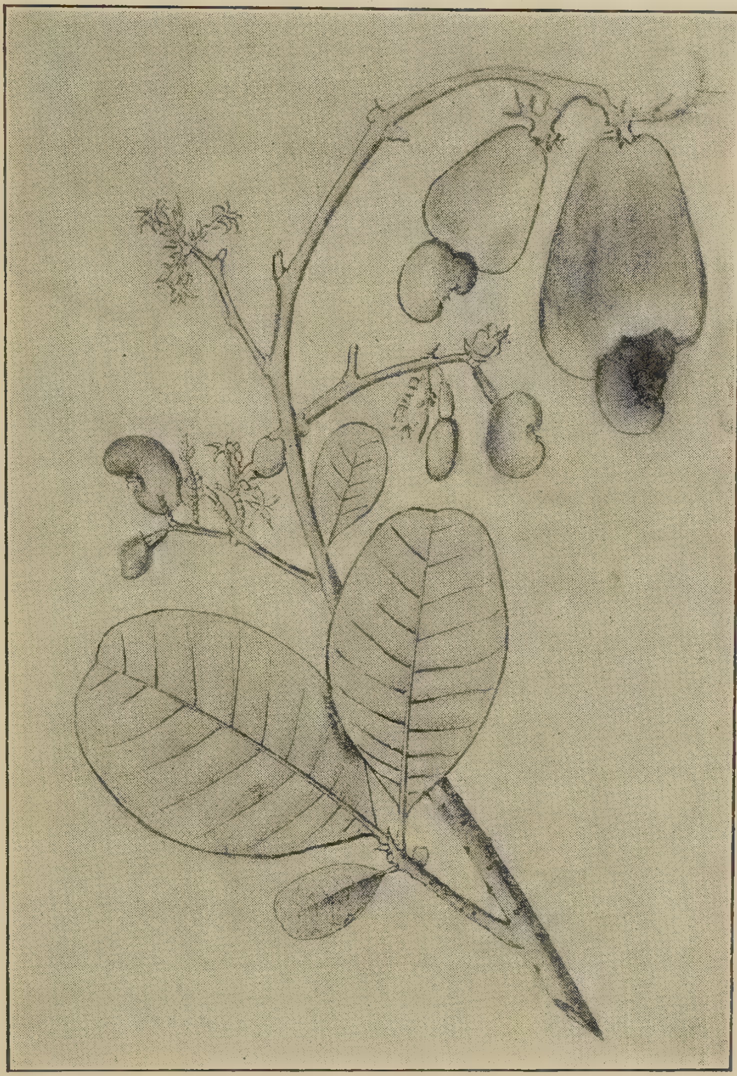

FIG. 68.—Cashew nut (*Anacardium occidentale*).

Kindt's * method of preparing the ink was to extract the nut with a mixture of absolute alcohol and ether and to evaporate the extract to the required consistence. The writing done with this fluid on the linen was moistened with lime water or an alkaline solution to turn it black. *Kindt* found that it was capable of

* *Dingler's polyt. Journ.*, 1859, cliv., 158.

resisting boiling with hydrochloric acid and potassium chlorate, though rendered faint by the treatment.

THE CASHEW NUT.—This is the fruit of another member of the *Anacardiaceæ*, *A. occidentale*, a tree somewhat resembling the walnut in size and appearance (Fig. 68). It is found in India, the West Indies, and tropical parts of South America.

The kidney-shaped fruit is about an inch in length, and projects from a fleshy pear-shaped fruit-stalk. The milky juice in the stem of the tree becomes hard and black on exposure to the air, and is used locally as a varnish.

Lewis * in 1763 found that the dark viscous juice within the nut when applied to cotton or linen gave a brown stain, which was very permanent, but did not become black upon exposure to the air.

The brown oil in the fruit is soluble in potassium hydroxide solution. On treating an alcoholic solution with basic lead acetate a red precipitate is obtained.

In 1847 *Staedeler* separated a vesicating principle, which he termed *Cardol* ($C_{21}H_{30}O_2$), and a reddish-yellow oil, which he termed *Anacardic acid.*

RHUS TOXICODENDRON.—This is a poisonous plant, originally indigenous to N. America, where it was known as the " poison tree " by the natives of Carolina,† and to Japan, where the juice has long been used as a varnish.‡

The milky juice rapidly darkens on exposure to the air, and has frequently been recommended as an indelible ink, especially for marking linen. Thus the *Abbé Mazeas* § stated that he had made experiments on this point, and found that the writing still remained black after five years, during which period the linen was repeatedly washed.

The plant, which is also known as the *poison ivy* and *poison oak*, grows to a height of several feet, and produces small green flowers (Fig. 69). The leaves are employed commercially in the manufacture of a black stain, and are collected for this purpose from May to July, while the plant is in bloom. The juice of the leaves will raise a blister on the skin within forty-eight hours, and even the vapours given off by the living plant, especially by night, produce vesicular eruptions on the skins of certain people peculiarly sensitive to its effects. *Porcher* found that the acrimonious vapours emitted during the night contained hydrocarbons, and would ignite when brought into contact with a flame.

* *Loc. cit.*

† Miller, *Trans. Roy. Soc.*, 1755, xlix., 161.

‡ *Ibid.*

§ *Loc. cit.*, xlix., 15.

Kluttel, who examined the constituents of the plant in 1858, found that it contained an "iron-greening" tannin.

In 1865 *Maisch* and *Stillé* * isolated a volatile substance which reduced silver nitrate solution and gave a white precipitate with

FIG. 69.—*Rhus toxicodendron.*

lead acetate, and a white precipitate, turning black on heating, with mercurous salts. To this substance they gave the name of *toxicodendric acid.*

Their results were confirmed in 1883 by *Pettigrew*, who also found that the acid gave a red colour with ferric salts.

* *National Dispensary*, p. 1382.

The black stain produced by the juice of *R. toxicodendron* cannot be removed by treatment with alcohol or soap and water, but dissolves in ether.

RHUS VENENATA.—This is a shrub which grows on marshy ground in North America, where it is popularly known as the *poison sumach.* It is usually from 10 to 15 feet high, but sometimes reaches a height of 30 feet. It has a dark grey bark, and produces greenish-white flowers and berries.

On making an incision in the bark a thick white, opaque, pungent fluid exudes, which on exposure to the air rapidly becomes black. When this liquid is boiled with water the volatile constituents are expelled, and the residue can be used as a black varnish similar to that prepared from the *Rhus vernicia* of Japan.

The poisonous symptoms caused by the juice are similar to those produced by *Rhus toxicodendron*, but many persons are quite immune to its effects, whilst others are more affected by its emanations than by those of *R. toxicodendron.*

The workmen who use it as a finishing varnish for boots frequently suffer from its action.*

RHUS RADICANS is a variety of *R. toxicodendron*, and not a separate species. It produces round greenish-white berries, and its juice has similar properties.

OTHER VEGETABLE JUICES.—*Lewis* in 1763 made numerous experiments to determine the permanence of the stains produced by the juices of different plants. He found that the milky juices of poppies, dandelion, hawkweed and sowthistle gave brown or brownish-red characters, but that these were readily removable on washing the linen.

The colourless juice from hop stalks, on the other hand, gave a very permanent pale reddish-brown stain.

Sloe Juice.—The juice from sloes used by itself gave a pale brown stain, whilst with the juice used in conjunction with alkali a much darker stain was produced. The fresh juice, on baking, became red, and when applied to linen gave red stains, which became blue on contact with soap. These characters were very permanent, and had only become faint after long continued washing.

In 1904 a new industry was started in Mexico, the pulp of the *Escleloahnitl* being then first made into marking ink on a commercial scale. The tree grows abundantly in the districts of Jalapa, Vinios, Texpoco, and Huaxtlau, and according to the report of the Consul † the trade was likely to be greatly developed. During the

* Millspauch, *American Medicinal Plants*, p. 37.
† *Board of Trade Journ.*, July 14, 1904.

month of April of that year 2,300 litres of the ink were exported to Germany.

According to *Stoneback* and *Calvert*,* the seeds of the avocado fruit (*Persea gratissima* and *P. drymifolia*), which is cultivated in Florida and California, contain a juice from which an indelible black ink used for marking linen is prepared.

Chemical Marking Inks.

SILVER INKS.—Of the different substances that have been employed as marking inks, the best known and most commonly used has been a solution of a silver salt, the reduction of which within the fibres of the material has left an insoluble black deposit of a more or less permanent nature.

The earliest inks of this type required the linen to be previously treated with what is known as a *pounce* and then dried, but these have been entirely superseded by inks which are reduced by passing a hot iron over the writing.

An ink of this earlier type was recommended by *Reimann* † as late as the year 1870. It contained 1·6 parts of silver nitrate, 2 parts of gum arabic, $\frac{1}{4}$ part of sap green in 16 parts of water; whilst the pounce consisted of 2 parts of crystalline sodium carbonate and 2 parts of gum in 8 parts of water.

A similar ink intended for use with steel pens was also described by *Reimann*. It was prepared by dissolving 2 parts of silver nitrate and $2\frac{1}{2}$ parts of gum in 5 parts of ammonia solution and filtering the liquid, a little magenta red being added to impart a temporary colour. The *pounce* for this ink contained 3 parts of sodium carbonate with $2\frac{1}{2}$ parts of gum in 9 parts of water.

Redwood's Marking Ink.—This was prepared by adding a solution of 31 parts of silver nitrate in water to a solution of 50 parts of sodium carbonate in water, collecting and washing the precipitated silver carbonate, triturating it with tartaric acid and adding sufficient ammonia solution to dissolve the silver tartrate. The ink was then completed by the addition of 15 parts of archil extract, 16 parts of white sugar, and 50 parts of gum arabic. With this ink no previous preparation of the fabric is necessary, a hot iron being passed over the writing to start the reduction.

Some time afterwards *Reade* (Eng. Pat., No. 11,474, 1846) claimed the use of a marking ink the basis of which was also silver tartrate. This was prepared by rubbing together in a mortar equal parts of

* *J. Amer. Pharm.*, 1923, xcv., 612.
† *Dingler's polyt. Journ.*, 1870, cxcv., 283.

tartaric acid and silver nitrate, then adding water, and finally neutralising the liquid with ammonia. In this process the somewhat tedious operation of washing the silver carbonate, as in *Redwood's* process, was dispensed with.

Claim was also made for the addition to this ink of an ammoniacal solution of a gold salt, so as to render the writing proof against the action of solvents for silver salts.

Dieterich (1897) recommends a solution of 25 parts of silver nitrate and 15 of gum in 60 parts of ammonia solution, with the subsequent addition of 2 parts of lamp-black or indigo as a temporary colouring matter.

The ink is used with a quill pen, and the writing is fixed by passing a hot iron over it. By increasing the amount of gum to 25 parts, a rubber stamp can be used with the ink.

Soubeiran's Marking Ink * consisted of 8 parts of silver nitrate, 4 parts of sodium carbonate, and 3 parts of copper nitrate, in 100 parts of ammonia solution.

Bufton (Eng. Pat., No. 738, 1856, *Prov.*) claimed the addition of platinum chloride to a silver marking ink, with the object of rendering the characters more permanent.

Kindt's Marking Ink † consists of 11 parts of silver nitrate dissolved in 22 parts of ammonia solution and mixed with a solution of 22 parts of sodium carbonate in 12 parts of water. The ink is then thickened by the addition of 50 parts of gum and coloured with 2 parts of sap green. Marks made with this ink on linen gradually darken on exposure to light, but the process of reduction is accelerated by heat.

Silver Chloride Marking Ink.—The linen fabric is first prepared with a 20 per cent. solution of sodium chloride, to which has been added 50 per cent. of gum arabic. The ink is prepared by dissolving 1 part of silver nitrate and 2 parts of gum in 10 parts of water, and adding a little indigo carmine as temporary colouring matter. The silver nitrate in the ink reacts with the sodium chloride in the prepared linen, forming silver chloride, which is reduced on exposure to sunlight.

Kuhr's Marking Ink.‡—Very black characters are produced by an ink consisting of 1 part of silver nitrate and 6 parts of gum arabic in 6 parts of water, on linen previously prepared with a solution of 1 part of sodium hyposulphite and 2 parts of gum in 16 parts of water.

* *Dingler's polyt. Journ.*, 1848, cviii., 157.
† *Ibid.*, 1859, cliii., 393.
‡ *Ibid.*, 1867, clxxxv., 326.

An analysis of a British silver marking ink made by the writer gave the following results:—Water (containing 4·87 per cent. of ammonia), 76·93; total solids, 23·07; mineral matter, 12·30; silver, 9·98; tartaric acid, 6·83; platinum, 0·26; substances insoluble in nitric acid, 0·11; and gum, 3·94 per cent. The ink contained archil as a temporary pigment.

GOLD MARKING INKS.—One of the best known gold inks is based on the formation of what is known as the *purple of Cassius*. The linen is prepared by treatment with a 1 per cent. solution of stannous chloride containing 10 per cent. of gum, whilst the ink consists of a 1 per cent. solution of the double chloride of gold and sodium, to which also has been added 10 per cent. of gum.

If the fabric is prepared with a 20 per cent. solution of oxalic acid containing 40 per cent. of gum, instead of with the tin solution, the gold writing has a metallic lustre after being ironed and washed.

Gold marking ink is more permanent than silver ink, and its addition to the latter was patented by *Reade* (*supra*).

PLATINUM MARKING INKS.—These are prepared in two solutions like the gold ink. The fabric is first treated with a mordant containing 30 parts of oxalic acid and 30 parts of gum in 100 of water and dried. The ink, which consists of 1 part of platinum chloride and 2 parts of gum in 10 parts of water, produces red marks on the prepared linen, which should be well washed as soon as the writing is dark enough.

A purple platinum marking ink described by *Reimann* (*loc. cit.*) contains 1 part of platinum chloride in 16 parts of water. The linen is first prepared with a solution of 3 parts of sodium carbonate and 3 parts of gum in 12 parts of water and dried. After the letters have been written on this prepared surface and have dried, the place is moistened with a solution of 1 part of tin chloride in 4 parts of water, which changes the writing to reddish-purple.

MARKING INKS CONTAINING OTHER METALS.—In addition to platinum and gold salts, which have been used either alone or in conjunction with silver salts as constituents of marking inks, and which are obviously too expensive for general use, numerous other metallic compounds have been employed for the same purpose. Thus in 1878 *Hickisson* (Eng. Pat., No. 5122) protected an ink containing a salt of vanadium with an oxidising agent composed of metals or salts, preferably those of nickel and copper, to act as mordants.

Sachs (Eng. Pat., No. 1838, 1880) has produced solutions which he claims to be good marking inks, by the action of polysulphides of heavy metals, such as those of iron, zinc, or copper, on organic

substances, such as non-volatile fats or sawdust, in the presence of a suitable metallic hydroxide or sulphide—*e.g.*, sodium hydroxide or sodium sulphide.

Marking inks of various colours were protected by *Langbeck* (Eng. Pat., No. 5946, 1882). These consisted of pigments, such as gas-black, vermilion, ultramarine, cadmium yellow, and emerald green, mixed with a suitable proportion of albumin, and incorporated with a liquid base composed of salicylic acid, turpentine oil, spirits of wine, glycerin, and water in approximately specified proportions.

In a subsequent patent (No. 751, 1883) taken out by *Hickisson* and *Langbeck*, the basis of the ink made from these pigments was a solution of india-rubber in carbon bisulphide, a little essential oil being added to prevent rapid evaporation. The fabric was heated after marking. In yet another method, protected by the same patentees (No. 752, 1883), the mixture of pigments and albumin was added to a base consisting of 5 to 8 grains of arsenic pent-oxide, 10 grains of turpentine oil, 6 drachms of glycerin, and 1 oz. of water.

Dimitry's Bichromate Marking Ink (Eng. Pat., No. 648, 1888) consists of a soluble colouring matter mixed with gelatin and potassium bichromate, this last constituent being reduced on exposing the writing to the action of sunlight.

Molybdic Marking Ink.—An ink was recommended by *Roder* * in 1856 as adhering well to the linen, and resisting the action of both acids and alkalies. It was prepared by dissolving 5 parts of molybdic oxide in sufficient hydrochloric acid, and adding 6 parts of gum arabic and 2 parts of sweetwood extract (*Lackritze*) in 30 parts of water. When the writing was dry the linen was treated with a solution of tin chloride.

Copper Marking Inks.—The precipitate obtained on treating a solution of copper chloride with potassium hydroxide is dissolved in as little ammonia solution as possible, and a little dextrin or gum added as a thickening agent. The writing done with this ink becomes black when a hot iron is passed over it.

Scoffern (Eng. Pat., No. 1744, 1859) protected a process of making an ink for marking cloth, paper, etc., by immersing organic fibrous material, such as silk, in ammonia solution containing copper, and admitting air through a small opening from time to time. The solution of silk in this "copperised ammonia" was described by the inventor as a "lustrous black ink."

A Blue Indelible Ink of American origin † consists of a mixture

* *Dingler's polyt. Journ.*, 1856, cxli., 159.
† *Scient. Amer. Suppl.*, June 31, 1902.

of a silver and a copper marking ink. (*a*) Silver nitrate 10 parts in 30 parts of ammonia solution. (*b*) Sodium carbonate 10 parts, gum arabic 15 parts, and copper sulphate 5 parts in 40 parts of water. The two parts (*a*) and (*b*) are mixed together.

Manganese Marking Ink.—Reimann (*loc. cit.*) recommends the following as a cheap brown marking ink. The linen is first prepared by treatment with a solution of 1 part of a ferrocyanide and ½ part of gum in 3 parts of water and dried. The writing is then done with a solution of 4 parts of manganous acetate in 12 parts of water, and the linen finally treated with a solution of 4 parts of potassium hydroxide in 10 parts of water.

This causes the separation of manganese hydroxide, which is gradually oxidised, forming a brown manganese oxide.

This process is manifestly too complicated for ordinary use, and the treatment of the linen with strong caustic alkali solution must have an injurious effect upon the fibres.

ANILINE MARKING INKS.—An ink in one solution is obtained by thoroughly mixing 2 parts of aniline black in 40 parts of strong alcohol (95 per cent.) containing 2 parts of hydrochloric acid, and adding a solution of 3 parts of shellac in 150 parts of the strong alcohol. The writing done with this ink is not removed by water, but is not very resistant to the action of alkalies.

*Jacobsen's Aniline Ink.**—This ink depends on the formation of aniline black within the fibres.

It consists of two solutions, which are kept separate until just before use :—

(*a*) *Copper Solution.*—Copper chloride, 8·52 grms. ; sodium chlorate, 10·65 grms. ; and ammonium chloride, 3·35 grms., in 60 c.c. of water.

(*b*) *Aniline Solution.*—Aniline hydrochloride, 20 grms., dissolved in 30 c.c. of water, and mixed with 20 grms. of a solution of gum arabic (1 : 2) and 1 grm. of glycerin.

For use, 1 part of (*a*) is mixed with 4 parts of (*b*). The writing on linen first appears green, and then gradually becomes black on exposure to the air. The change takes place at once on heating the fabric, but it is advisable to hold it over steam, since dry heat tends to render the marked places brittle. Finally the place should be washed in soapy water, which renders the writing blue-black. Marking properly done with this ink resists the action of acids and alkalies, and can be frequently washed without being rendered much fainter.

Another ink of the same type, suitable for use with stamps, is

* *Dingler's polyt. Journ.*, 1867, clxxxiii., 78.

given by *Desmarest* and *Lehner* * :—A. Copper chloride, 1 ; ammonia solution, 40 ; sodium chloride, 1 parts. B. Aniline hydrochloride, 40 ; gum, 15 ; glycerin, 15 ; and water, 30 parts.

Four parts of A are mixed with 1 part of B immediately before marking, and the writing ironed and left for some minutes.

According to *Strunk*,† textile fabrics marked with aniline inks are liable to injury when sterilised by steam unless the excess of ink has been washed out previously, and even in that case woollen articles are rendered friable in the marked places by steaming.

Silver inks do not injure the fabric on sterilising, provided that the markings are exposed to sunlight for twenty-four hours and then steamed for 30 minutes.

There are also several preparations on the market in which the aniline salt and the oxidising agent are present in one solution, but are so balanced that oxidation does not take place within the bottle. The ink thus remains fluid until it is applied to the fabric, but then its more volatile constituents evaporate and oxidation takes place with the formation of the black pigment.

The exact composition and methods of preparing these inks are carefully guarded as trade secrets.

In some of them there is an excess of free aniline over the oxidising agent, and this evaporates when the ink is put upon the fabric. Others contain both free aniline and acetic acid, both of which subsequently evaporate.

The stage of suspended oxidation is by no means easy to reach, and an ink may keep well for a month or so in the bottle and then suddenly yield a granular deposit of aniline black, or gelatinise into a sticky mass that is useless for marking purposes.

Grawitz's Patent Inks.—Aniline inks in one solution have been patented by *Grawitz* (Fr. Pat., No. 276,397, 1898). One of these is made as follows :—

(*a*) Aniline hydrochloride, 135 grms. ; aniline oil, 200 c.c., and hot water 5 litres.

(*b*) Sodium chlorate 400 grms. in 3 litres of hot water.

The solutions (*a*) and (*b*) are mixed and cooled, and the copper sulphide precipitated from 250 grms. of copper sulphate added. Or copper thiocyanate or other salt promoting the oxidation may be used.

Another of *Grawitz's* inks contains :—

(*a*) Aniline oil, 110 c.c. ; hydrochloric acid (20° Bé.), 100 c.c. ; water, 100 c.c.

* *Loc. cit.*, p. 209.

† *Chem. Zeutralbl.*, 1911, i., 463.

(*b*) Potassium ferrocyanide, 150 grms. in 300 c.c. of boiling water. The two solutions are mixed, cooled, and a solution of 60 grms. of sodium chlorate in 400 c.c. of water added.

In these inks the conditions for stability do not appear to have been realised, for in the writer's experiments the inks speedily became solid in the flask.

INDIGOTIN MARKING INKS.—The so-called indigo blue when pure is known in chemistry as *indigotin* ($C_{16}H_{10}N_2O_2$). When this is treated with a reducing agent it is converted into a colourless compound, *indigo white* ($C_{16}H_{12}N_2O_2$), which is readily soluble in solutions of alkalies, and has only to be exposed to the air to be gradually oxidised again into the insoluble blue compound.

An indigo marking ink based on this reaction is prepared by treating a mixture of 20 parts of indigo blue powder and 40 parts of ferrous sulphate with a solution of 40 parts of sodium hydroxide in 200 parts of water. The whole is then left for several days in a well-corked bottle, which is shaken from time to time until the reduction is complete, and all sign of blue has disappeared. The liquid is then decanted, and 20 parts of gum arabic added to 1 part of a saturated solution of litmus to form the provisional colouring-matter. The writing done with this ink is soon oxidised by the atmospheric oxygen, and eventually becomes deep blue. The same oxidation gradually takes place in the ink, with the formation of a blue deposit in the bottle.

A marking ink patented by *Johnson* (Eng. Pat., No. 1771, 1880) is based on the synthetical formation of indigo blue within the fibres of the fabric. The material is treated with a solution containing ortho-nitro-phenyl-propiolic acid, a reducing agent such as glucose, and a fixed caustic or carbonated alkali. The writing is developed by the action of steam, which produces a blue colour, or by dry heat, which makes it black.

ALIZARINE MARKING INK.—A red marking ink, containing the pigment of madder (alizarine) as its basis, was patented by Möller in 1864 (Eng. Pat., No. 2511). The linen was first prepared by treatment with a solution of alum, and the marking done with an ink composed of an alcoholic extract of madder with an alkali salt, gum, and vermilion.

CONGO RED MARKING INK.—A red marking ink is described by *Gouillon.** It is prepared by dissolving 1 grm. of caustic soda in 200 c.c. of water and 10 grms. of glycerin, and adding to the hot solution 5 grms. of Congo Red and 30 grms. of Senegal gum. It is then left to clarify.

* *Fabrication des Encres et Cirages*, Paris (1906), p. 161.

The markings done with this ink disappear after a few washings.

EXAMINATION OF MARKING INKS.—The chief essentials of a good marking ink are:—(1) It shall not injure the fibres of the fabric; (2) it shall not be too viscous to flow smoothly from the pen, and yet not so fluid as to "run" when applied to the linen; (3) it shall produce characters which rapidly darken when treated with a moderately hot iron or otherwise; (4) the character shall not fade when repeatedly washed with soap and water, and shall resist the action of acids, alkalis, and bleaching-powder; (5) it shall be stable in the bottle, and not gelatinise or form deposits if the cork is not replaced for some time.

The composition of an ink is of subsidiary importance as compared with the results of practical tests. It is best to make characters both on linen and fine fabric, and to follow the manufacturer's directions for the subsequent treatment of the material.

MARKING INK PENCILS.—The earliest pencils intended for marking linen contained a silver salt incorporated with a suitable basic material and a provisional colouring matter. In *Dunn's* patent (Eng. Pat., No. 2316, 1858) plumbago is mentioned as a suitable substance to be mixed with the silver salts.

A similar pencil was patented by *Schroll* (Eng. Pat., No. 379, 1877). This was composed of a suitable clay earth mixed with silver nitrate or other soluble silver salt, and plumbago freed from impurities that would cause reduction in the silver salt.

In 1878 *Hickisson* (Eng. Pat., No. 5122) adapted his vanadium marking ink (*supra*) to the preparation of marking ink pencils, gum, gelatin, dextrin, clay, or other suitable substance being added, and the mass moulded into the required shape.

Marking pencils, giving different coloured characters, were prepared by *Hickisson* and *Langbeck* (Eng. Pat., No. 752, 1883) from the marking inks containing a suitable pigment and albumin in a liquid base of arsenic pentoxide, turpentine oil, glycerin, and water.

A silver pencil also patented by *Hickisson* (Eng. Pat. No. 9149, 1884) has a marking-point which may consist of silver nitrate and potassium nitrate, or in some cases ammonium carbonate, fused with gum, whilst the other end of the pencil contains a mordant composed of, *e.g.*, borax, wax, and pyrogallol, which is applied to the writing to fix it. In a subsequent patent (Eng. Pat., No. 15,961, 1884), claim is made for separate pencils containing only the mordant. Aniline dye-stuffs soluble in oil, claimed by *Hickisson* (*supra*) are also made the colouring material in marking pencils. For this purpose they are incorporated with suitable ingredients,

such as gum tragacanth, kaolin, and borax, into a solid mass. The linen fabric is damped with a suitable oil, such as castor oil, and the writing finally heated.

In our experience with certain marking ink pencils of foreign origin containing aniline dye-stuffs, the writing is of a very fugitive character.

CHAPTER XIV.

SAFETY INKS AND PAPERS.

THE term "safety" has been frequently applied to inks which are supposed to resist the action of all chemical agents not sufficiently powerful to destroy the paper or parchment itself. The importance of such an ink in the case of historical records or legal documents, etc., is obvious, and numerous experiments have been made to discover the best fluid for the purpose.

It has already been noted in the introduction that iron gall inks may, under favourable conditions, almost equal carbon inks in defying the ravages of time, although many instances can be cited where inks of the same character have prematurely faded. It may be pointed out in connection with this imperfection that chlorine is used as a bleaching agent in paper manufacture, and although "antichlor" (sodium thiosulphate) is used to remove free chlorine, cases may occur in which a trace of the chlorine is left, and would then have an effect upon an iron ink.

VARIOUS SAFETY INKS.—Several of the earlier formulæ for producing permanent writing fluids have already been described in Chap. i., in the section dealing with carbon inks, p. 34.

Inks recommended by French Commission.—In 1831 a Commission appointed by the Paris Académie des Sciences, and including such eminent chemists as Gay-Lussac and Chevreul, made a critical examination of all the inks that had been proposed up to that time for the prevention of the falsification of writing, and concluded that prior to 1826 none was satisfactory. They were either too thick, or attacked the paper, or yielded a deposit too readily. Of the different inks submitted, the Commission recommended the two following:—

(i.) Indian ink (4 to 5 grms.) mixed with 1,000 grms. of dilute hydrochloric acid (2·010 sp. gr.). This ink flowed well and had good penetrating power, whilst the acid did not injure the paper.

(ii.) A solution of manganese acetate (sp. gr. 1·074). With a ninth of its volume of acetic acid (100 parts neutralising 160 of sodium carbonate), thoroughly incorporated with Indian ink. The writing was then fixed and rendered indelible by holding it over ammonia vapour.

The advantage of this ink over the preceding one is that the paper will not contain free acid.

We have prepared carbon inks from these formulæ, and find that the writing resists the action of water, acids, and bleaching agents. In the case of the first ink, however, we find the quantity of Indian ink mentioned quite insufficient. We used the finest that we could obtain, and had to add at least six times as much in order to obtain characters of sufficient blackness. After the treatment with ammonia vapour the writing becomes much greyer.

MacCulloch * used a solution of potash and wood tar, whilst *Thomson* † mixed lamp-black with a solution of shellac and borax.

RESINOUS INKS.—This last ink is very much on the lines of that described by *Desmarest* ‡—viz., shellac, 15; borax, 8; gum arabic, 8; lamp-black, 10; and water, 130 parts.

The powdered shellac and borax are boiled with the water, and the solution mixed with the powdered gum and lamp-black, and subsequently decanted from the heavier particles.

In 1837 *H. Stephens* and *E. Nash* patented (Eng. Pat., No. 7342) the addition of carbonaceous matter to saline or alkaline solutions of resinous substances to form compounds not attacked by ordinary chemical agents (*vide infra*).

An ink of this character is prepared by boiling 10 parts of ordinary rosin and 10 parts of sodium, potassium, or ammonium carbonate, either alone or, preferably, mixed in equal proportions, with 100 parts of water, and adding a mixture of 4 parts of powdered gum, and 2 parts of lamp-black.

TRAILL'S CARBON GLUTEN INK.§—This consisted of lamp-black and indigo incorporated with an acetic acid solution of the gluten of wheat flour. The gluten was prepared by kneading the flour in a current of water until the starch had been separated. After twenty-four to thirty-six hours in the water it was digested with acetic acid (sp. gr. 1·033 to 1·034) in the proportion of 20 to 3 of gluten. The grey liquid eventually obtained with the aid of

* *Ann. de Chim. et Phys.*, 1831, xlviii., 5.

† *Ibid.*

‡ *Les Encres et Cirages*, 1895, p. 141; *Manuel Pratique de la Fabrication des Encres*, 1923, p. 122.

§ *Trans. Roy. Soc. Edin.*, 1840, xiv., 426.

gentle heat was then used as the medium for the pigment, which consisted of about 2 per cent. of purified lamp-black and about ½ per cent. of indigo.

An ink attributed to *Herberger* is essentially identical with that devised by *Traill.*

Traill states that his ink was at once adopted (1840) by the National Bank of Scotland, which had recently been the victim of numerous forgeries, in which the ink on bills, etc., had been erased and other figures substituted. As a matter of interest we made inquiries from the present authorities of that bank in Edinburgh, who kindly informed us that they had no record of any other ink than ordinary iron gall ink having been used by them. It is not improbable that the use of *Traill's* carbon ink was discarded on the introduction of cheques printed with special inks, which would change colour if any chemical were used to remove the writing.

BAUDRIMONT'S SOLUBLE GLASS INK.*—This is an intimate mixture of soluble glass (sodium silicate) with 10 per cent. of lamp-black. The silica, on separating from the ink during the drying, encloses particles of carbon, thus rendering the characters permanent. It is advantageous to remove the sodium carbonate formed by the action of the carbon dioxide in the air upon the sodium oxide by first treating the written paper with dilute acetic acid, and then thoroughly washing it with water.

We have found that the ink thus prepared from commercial sodium silicate is much too thick for use, and requires to be suitably diluted with water. Ink having a specific gravity of 1·270 flows freely from the pen and gives very black writing. When the dried characters are treated with water the surface ink is readily washed off, but there still remains a greyish writing within the fibres of the paper, and this is not removed by leaving it in water for twenty-four hours. If the writing is left for twelve hours before immersion in water much less of the pigment is removed. The ink can be blotted immediately after writing without rendering it too pale. It is not affected by acids, alkalis, or chlorine.

OTHER CARBON INKS.—Numerous other formulæ have been given for the preparation of inks of this character, but most of them are only later modifications of those described above. Thus, a weak solution of sodium hydroxide is used instead of hydrochloric acid as a medium for Indian ink (*Bezanger*); and another ink consists of lamp-black and gum arabic incorporated with a dilute solution of oxalic acid.

* Desmarest, *Les Encres et Cirages*, p. 144.

This latter ink has not much penetrating power, and the writing can be removed from the paper by careful washing with water.

Whitfield (Eng. Pat., No. 7474, 1837) prepared lamp-black from a mixture of linseed oil, Venice turpentine, and other organic substances, by firing the mass with a hot iron, and collecting the soot in an inverted cone. 1 lb. of this lamp-black was mixed with 1 quart of vinegar, 2 galls. of hot water, $\frac{1}{4}$ lb. of gum, and $\frac{1}{4}$ lb. of shellac, and the whole boiled for ten minutes. Powdered galls (1 lb.) and logwood chips (2 lbs.) were then introduced, and the ink stirred until cold, and exposed for three weeks to the atmosphere in flat pans.

In other inks there is a basis of colloidal carbon, and these have the advantages that the carbon in this form penetrates well into the paper, and that deposits are not readily formed in the ink when kept.

SAFETY PAPERS USED WITH SPECIAL INKS.—*Traill* (*loc. cit.*), in the course of his experiments, tested the permanence of the writing produced by different solutions of metallic salts on specially prepared papers. Sheets of unsized paper were soaked in the following different solutions, and then dried :—(i.) An infusion of galls ; (ii.) a solution of potassium ferrocyanide ; (iii.) sodium chloride solution ; (iv.) sodium phosphate solution ; (v.) potassium iodide solution ; and (vi.) potassium dichromate solution.

(i.) Characters on this paper made with iron sulphate or copper sulphate were readily removed by chlorine, oxalic acid, etc.

(ii.) *Ferrocyanide Paper.*—Antimony chloride solution gave bright blue characters, which resisted the action of chlorine, but were effaced by ammonia. Iron sulphate gave dark-blue writing, copper sulphate brown characters, and cobalt nitrate deep-brown characters, which resisted the action of alkalis, but were bleached by chlorine.

(iii.) *Sodium Chloride Paper.*—The characters produced by silver nitrate on this paper were removed by ammonia.

(iv.) *Sodium Phosphate Paper.*—Acetate of lead produced intense yellow characters.

(v.) *Metallic iodides* formed in the paper were equally unreliable, as was also the case with chromates.

(vi.) *Metallic sulphides*, whether precipitated in the paper or added in the form of coloured compounds (lead sulphide), to ordinary inks, were easily bleached by chlorine.

Indigo sulphate was also bleached by chlorine, but when added to an ordinary iron gall ink increased its stability.

Antimony and Cobalt Salts Mixed.—A mixture of cobalt nitrate and antimony chloride ground together and mixed with gum water

yielded an ink which gave dark-brown characters on ferrocyanide paper. The writing was weakened, but not destroyed, by acid or alkali; but when soaked alternately in these reagents was completely effaced.

Summarising the behaviour of different reagents on the metallic compounds tried, *Traill* came to the following conclusions:—(i.) *Chlorine* bleached all with the exception of the blue precipitate formed on adding antimony chloride to potassium ferrocyanide. (ii.) *Oxalic acid* completely bleached gall ink, Prussian blue, lead iodide, mercury iodide, lead chromate, and indigo sulphate, though the last offered more resistance. (iii.) *Antimony chloride* weakened or destroyed all the metallic characters with the exception of the antimony ink. Indigo, again, offered considerable resistance. (iv.) *Caustic alkalis* destroyed all with the exception of the salt formed by adding cobalt nitrate to potassium ferrocyanide.

PATENT PERMANENT INKS.—The addition of finely divided carbon to ordinary writing inks has been claimed in numerous patents—*e.g.*, by *Scott* in Eng. Pat., No. 8770, of 1840, who added gas-black, indigo and Prussian blue to gall and logwood ink. In *Reade's* patent, No. 11,474, of 1846, the use of Prussian blue was also claimed.

An indelible ink patented by *Stephens* and *Nash* in 1837 (Eng. Pat., No. 7342) was prepared by distributing the carbon in a solution of a resinous soap; whilst *Melville* (Eng. Pat., No. 534, 1860) claimed an ink consisting of plumbago, with resin, gum, alum, and a suitable colouring matter. In 1861 *Stevens* (Eng. Pat., No. 2972) patented an indelible anti-corrosive ink which consisted of solutions of aniline dyes mixed with finely divided carbon. The ink protected by *Gaffard* (Eng. Pat., No. 1839, 1874) was composed of a mixture of carbon with the solution of an alkali silicate.

A mixture of sugar, aniline black, and soot in logwood extract form the constituents of *Fonseca's* patent ink (Eng. Pat., No. 859, 1883); whilst *Wass* (Eng. Pat., No. 9249, 1885) employs carbonised sugar scum as the source of the carbon. A solution of soap in water or other medium is claimed by *Lichtentag* (Eng. Pat., No. 24,644, 1898) as the liquid part of a carbon ink.

Only a few inks of this class not containing carbon have been patented. *Ellis* (Eng. Pat., No. 2267, 1865) claimed that an indelible ink was produced by precipitating colouring matter by means of silicic acid, and dissolving the precipitate in a suitable silicate solution. In 1891 *Leech* and *Harrobin* (Eng. Pat., No. 1616) protected a writing fluid consisting of turpentine, asphalt, resin, alum, beeswax, and colouring matter.

Aluminium powder with a protective varnish forms the basis of *Blancan's* indelible ink (Eng. Pat., No. 7263, 1893).

The use of the colloidal mill for the preparation of finely divided pigments is claimed by *Plauson* (Eng. Pat., No. 187,732, 1922).

PATENT SAFETY PAPERS.—One of the earliest so-called "safety" papers was that described by *Stevenson* (Eng. Pat., No. 7313, 1837). This consisted of paper impregnated with a solution of manganese chloride and potassium ferrocyanide, and was stated to be stained by any chemical that would remove ink.

Ballande's safety paper was impregnated with mercuric chloride, or a salt of iron or copper, whilst the ink consisted of a solution of sodium thiosulphate with alum, or alkali or alkaline salts, or of other salts (*e.g.*, iodides, sulphocyanides, etc.) capable of forming coloured insoluble compounds within the paper. (Eng. Pats., No. 861, 1859, and 388, 1860).

In 1864 *Baildon* (Eng. Pat., No. 2223) claimed the use of a safety paper from which the colour was discharged by acid in the special ink to be used. A patent on similar lines (No. 6938) was published by *Thacker* in 1895, the paper in this case being coated with colour, which was removed as soon as it came in contact with the ink.

It is interesting to note that the colour of ordinary blue paper such as is used for official and commercial purposes is discharged by dilute mineral acid; and we have good authority for stating that acid was actually in use as a white ink on that kind of paper some years before the date of *Baildon's* patent.

CHAPTER XV.

SYMPATHETIC INKS.

CONTENTS.—History—Various sympathetic inks—Patent sympathetic inks—Examination of documents for secret writing.

HISTORY.

THE term *sympathetic ink* is applied to writing fluids which yield characters that remain invisible until heated or treated with some suitable reagent. Such inks appear to have been known in the early days of the Roman Empire, for *Ovid* mentions milk as a suitable liquid, whilst *Pliny* refers to the juice of different plants.

The earliest known chemical sympathetic inks were regarded as acting by magnetism. Thus *Brossonius*, writing in a medical treatise in the early part of the seventeenth century, describes a " magnetic fluid " made from " arseniated liver of sulphur," and only visible when looked at with " eyes of affection." This appears to have been nothing more than an ink of lead acetate, the characters being rendered visible by the action of hydrogen sulphide.

Borel * also describes these inks, the secret of which he learnt from *Brossonius*, as *aquæ magnetice e longinquo agentes*, but points out that there is nothing miraculous in their action. They are also alluded to by *Robert Boyle* (1663) and by *Otto Tachen* (1669), who denied that there was anything magnetic about them, and by numerous later writers.

The name *sympathetic* appears to have been first used by *Le Mort* to describe the lead acetate ink, and the term was subsequently applied to all secret inks of the same kind.

In 1715 *Waiz* discovered the use of solutions of cobalt salts as sympathetic inks, and the French chemist *Hellot* also gave a description of them a few years later.

Battista Porta (1567) described various kinds of invisible inks, such as, for example, the use of a solution of iron sulphate to be made visible by sponging the writing with a decoction of galls. He also alluded to a colourless ink which was made visible by dusting the paper with a certain black powder.

* *Historiarum Centuriæ*, iv., p. 110.

Lemery (1720) describes sympathetic inks which appear to consist of lead acetate, the writing being made visible by the application of a sulphide.

VARIOUS SYMPATHETIC INKS.—The change in the colour of characters written with a solution of cobalt chloride is due to the fact that the pink salt loses part of its water of crystallisation when heated to 120° C., forming a blue compound, and that the latter on exposure to the air gradually absorbs water, and regains the pink colour, which is nearly invisible on white paper. By the addition of other salts to the cobalt solution—*e.g.*, nickel sulphate—the colour of the heated characters is modified.

Cobalt thiocyanate solutions give pale red writing, which changes to blue on heating.

The following table gives a list of some of the better known substances used as sympathetic inks :—

Colour.	Ink.	Mordant.
Black or brown.	Lead acetate. Mercuric chloride. Galls. Pyrogallol. Silver salt.	Hydrogen sulphide. Stannous chloride. Iron sulphate. An alkali. (Action of light).
Blue.	Starch. Cobalt nitrate. Iron sulphate.	Iodine. Oxalic acid. Potassium ferrocyanide.
Yellow.	Copper chloride. Basic lead acetate. Antimony chloride.	(Yellow on heating). Hydriodic acid. Galls.
Green.	Cobalt chloride with a nickel salt. Potassium arsenate.	(Action of heat). Copper nitrate.
Purple.	Gold chloride.	Stannous chloride.
Gold.	Gold sodium chloride.	Oxalic acid (10 per cent.) On treating with hot iron metallic lustre is produced.

A sympathetic method might be based on a process familiar to photographers, by which so-called "magic pictures" have been produced. A photographic print on bromide paper after being bleached in a solution of mercuric chloride and thus rendered invisible, is again made apparent by being placed in contact with blotting paper moistened with a solution of sodium thiosulphate ("hypo"). It is obvious that writing executed with any suitable developer on bromide paper would appear and disappear under similar conditions.

Another method is suggested by the fluorescence of a solution of a quinine salt under ultra-violet light, or of other compounds under the influence of radium, X-rays, etc.

Sympathetic inks have frequently been put to an ingenious and perverted use by sharpers of the racecourse, two of whom were convicted of this kind of fraud a few years ago. A betting paper giving the names of horses, etc., is written in two kinds of ink, one of which fades away, whilst the other gradually appears. The disappearing ink commonly used is a weak solution of starch tinged with a little tincture of iodine, and writing done with this soon fades away, whether exposed to the light or not.

The ink used for the invisible writing is often an ammoniacal solution of silver nitrate, which gradually darkens under the influence of light. Fugitive dyes have also been used as disappearing inks, such as—*e.g.*, quinoline blue and furfuraniline, the solution of which gives magenta writing, which soon fades away under the influence of sunlight.

On the other hand, invisible inks have been used in the interests of the law. On several occasions during the last few years certain districts have been victimised by an epidemic of anonymous letters. When all attempts to fix the writers have failed, stamps marked with invisible ink have been supplied to suspected households. In several instances the ruse has proved successful, and further letters bearing the marked stamps have been stopped in the post and the identity of the writers established.

During the war the use of sympathetic inks for communicating valuable information to the enemy was the subject of several trials, and some details of the methods used were published in the press. Lemon juice was used for the purpose by *Kuepferle*, and at his trial in 1915 evidence was given that a pen nib showed indications of fruit juice, whilst a reaction for iron was obtained in the examination of a cut lemon found in his possession.

The use of saliva as an invisible ink was well known to the Germans long before the war, and a description of the method of

developing saliva writing with ink is given by *Dennstedt* and *Voigtländer*,* although it does not seem to have been described in any English text-book.

Writing in saliva or other physiological fluid may conveniently be developed with any suitable writing ink diluted with a large volume of water. It has been pointed out on a previous page (p. 184) that the darkening of ink is accelerated by the presence of saliva, possibly through the agency of an enzyme, so that if the paper is brushed over with dilute ink the portions written in saliva will appear in dark characters long before the ink spread over the rest of the paper darkens.

PATENT SYMPATHETIC INKS.—Although sympathetic inks are usually regarded as only scientific toys, they have been applied to several practical purposes, and have been made the subject of different patents.

In the Eng. Pat., No. 2389, of 1877, *Kromer* describes a process for detecting any tampering with envelopes, which consists in separating the two constituents of a sympathetic ink by the adhesive gum, so that should steam be applied to open the envelope the two substances come in contact and form an ink, leaving a stain upon the paper. A similar device was patented by *Pulford* (Eng. Pat., No. 15,565, 1889).

Claim is made for the use of dichromate solution in Eng. Pat., No. 3657, of 1881, the characters being made visible by the action of light.

Quelch (Eng. Pat., No. 7472, 1888) has protected a method of writing with a saturated solution of potassium nitrate on a non-glazed surface, a part of the writing being afterwards touched with a red-hot wire. Papers thus treated are sold as toys for children.

A sympathetic ink claimed by *Himly* (Eng. Pat., No. 730, 1887) consists of a solution of platinum magnesium cyanide with a suitable medium, such as gum, gelatin, etc. When exposed to damp air this changes to pink, the colour disappearing on applying heat.

An invisible ink claimed by *Tschofen* (Eng. Pat., No. 2130, 1890) consists of a mixture of chalk or similar substance with water, which is used for writing on a glazed surface, the characters being subsequently dusted over with graphite, bronze powder, etc., to render them visible.

Adams (Eng. Pat., No. 3459, 1896) has patented the use of dilute sulphuric acid (1 : 17) as an invisible ink, the writing being rendered permanently visible on heating the paper so as to bring about surface carbonisation.

* *Lehrbuch der Gerichtlichen Chemie*, 1907, p. 122.

Another sympathetic ink which only becomes visible on heating the paper is described by *Möller* in Eng. Pat., 21,991, 1897. It consists of about 100 parts of alum and 100 parts of white garlic juice. The writing is rendered visible by heating the paper and cannot be removed by water.

In *Kretschmann's* patent (No. 6727, 1899) paper is treated with a solution of cobalt chloride, and a solution of rock-salt used as ink. On heating the paper the writing appears in pale green characters. In order to detect tampering certain signs are made on the paper with a solution of resorcin and paratoluidine, and these on heating change from red or yellow and become permanently black or brown. In a subsequent patent (No. 7367, 1900) *Kretschmann* has claimed a process of treating paper with a non-hygroscopic salt of cobalt (such as the basic carbonate), and writing on it with a solution of salt and a substance such as vinegar, which will convert the salt in the paper into a hygroscopic salt.

The sympathetic process described by *Bachem* (Eng. Pat., No. 8976, 1899) consists of the use of two substances, such as cobalt chloride and magnesium platino-cyanide, in two layers, one of which becomes visible on heating, while the other simultaneously disappears.

In the patent process of *Garzino* (Eng. Pat., No. 9108, 1908) the ink consists of an alkaline solution of potassium ferrocyanide, the alkali being added to prevent the development of Prussian blue from any iron in the paper. Graphite is added to make the characters visible at the time of writing, but is subsequently removed by india-rubber. The writing is developed with solutions of iron, alum, and potassium bisulphate, the object of the latter being to act as a mordant and prevent smudging on the application of the iron salt.

Examination of Documents for Invisible Writing.—Apart from the application of heat and light, it is obvious that many chemical reagents must be applied to discover the presence of invisible writing. These are applied on the end of a feather to various parts of the document.

The use of iodine vapour as a general reagent for developing secret writing was described by *Hager*, whose methods are quoted by *Guareschi*.* It will detect many substances, although not all.

It is quite an easy matter to ascertain whether in the case of invisible writing done with a cobalt salt the chloride or the nitrate was used. If a drop of silver nitrate is placed on one of the letters and examined under the microscope an opalescence will gradually

* *Gli. Inchiostri da Scrivere*, 1915, p. 130.

spread through the drop if chloride was present. Again, if a minute drop of sulphuric acid and a few particles of brucine are applied to another letter a blood-red coloration will indicate the presence of a nitrate.

Further particulars of the methods of examining documents for secret writing are given in the writer's book on documents.*

* *Documents and their Scientific Examination*, 1922, p. 153, *et seq.*

CHAPTER XVI.

INKS FOR MISCELLANEOUS PURPOSES.

INK POWDERS AND TABLETS.

THE earliest methods of preparing a powder which would yield an ink on the addition of water consisted in mixing together the finely powdered ingredients of the ink. Thus *Canneparius* * in 1660 describes an ink powder containing equal parts of finely powdered galls and ferrous sulphate with a sufficient quantity of gum and shellac. Obviously, ink thus prepared would be very pale and of poor quality.

A later method was to evaporate a good iron gall ink to dryness, and to mix the powdered residue with water as required. The disadvantage of this process is that the pigment is rendered insoluble by the evaporation, and that the ink prepared again from the powder contains particles suspended in water instead of being in solution. This objection also applies to *Leonhardi's* † ink tablets, which were prepared in a similar fashion.

Dieterich uses his oxidised tannin extract (p. 117) as the basis of portable gall ink powders.

LOGWOOD INK POWDERS.—An old Austrian patent taken out by *Platzer* ‡ claimed the use of a powdered ink, consisting of 100 parts of logwood extract with 1 part of potassium dichromate and 10 parts of sodium sulphindigotate.

Cooley (Eng. Pat., No. 106, 1867) made claim for ink powders yielding ink of different shades and containing logwood extract or

* *De Atramentis*, 1660, p. 273.
† *Dingler's polyt. Journ.*, 1856 cxlii., 446.
‡ *Ibid.*, 1859, cliv., 158.

hæmatoxylin with various salts. Thus powdered logwood extract with potassium chromate and dichromate yields inks of different shades of brown, whilst by adding potassium carbonate to the chromate a rich blue-black ink is produced, the colour being further modified by the addition of alum. The use of copper acetate in place of alum gives a blue-black shade; and by using tin chloride, chrome alum or manganese sulphate in place of potassium chromate various shades of purple are produced.

Dieterich * gives the following directions for making logwood ink powders :—

Red Logwood Ink.—Logwood extract, 100; aluminium sulphate, 40; potassium oxalate, 40; potassium bichromate, 3; and salicylic acid, 1·5 parts, in 1 litre of water.

Violet Logwood Ink.—Logwood extract, 100; aluminium sulphate, 40; potassium oxalate, 60; potassium bisulphate, 10; potassium chromate, 5; and salicylic acid, 1·5 parts.

ANILINE INK POWDERS.—Owing to the readiness with which they dissolve in water, certain aniline dye-stuffs are particularly suitable for the purpose of ink powders.

Viedt in 1875 recommended the use of nigrosine, which was to be dissolved before use in 80 parts of water; and since then aniline dye-stuffs have formed the basis of numerous English patents (*vide infra*).

Dieterich (*loc. cit.*) has also described ink powders of different colours prepared from aniline dye-stuffs :—

Black Ink Powder.—Aniline green D., 9; Ponceau R.R., 8·0; phenol blue, 1.

Red Ink Powder.—Ponceau red, R.R.

Green Ink Powder.—Aniline green.

Violet Ink Powder.—Phenol blue, 1·5; Ponceau R.R., 2·0 parts.

Blue-green.—Phenol blue, 1·5; Aniline green, 2·5 parts.

For copying ink powders greater proportions of colouring matters to water must be used and sugar added, *e.g.* :—

Violet Copying Ink Powder.—Methyl violet, 20; sugar, 10; and oxalic acid, 2 parts.

Red Copying Ink Powder.—Eosine, 15; and sugar, 30 parts.

Blue Copying Ink Powder.—Resorcin blue, 5; sugar, 20; and oxalic acid, 1·0 parts.

PATENT INK POWDERS AND DRIED INKS.—The earliest patent for an ink powder was taken out by Holman in 1668 (No. 258), but no details of the method of preparing the substance are given. After that date no patent seems to have been applied for

* *Loc. cit.*

until 1867, when *Cooley* (Eng. Pat., No. 106) claimed the use of various dry extracts of dye-stuffs and salts, such as extract of Brazil wood with salts of tin, alum, tartrate, alkali or acid; Prussian blue, soluble indigo with suitable mordant; sap green, with or without alum; saffron with alkali carbonate; extract of French berries with alum; and powdered galls or pyrogallol or a mixture of these with ferrous sulphate.

Byford's Ink Powder (Eng. Pat., No. 974, 1876) contained logwood extract, indigo sulphate, and ferrous sulphate.

In 1878 *Jacobsohn* (Eng. Pat., No. 1586, *Prov.*) described an ink powder for copying, which consisted of a solution of an aniline dye-stuff, with sugar, gum arabic, and glucose evaporated to dryness.

Payne's tablet for inking rubber stamps (Eng. Pat., No. 3179, 1886) consists of glycerin, gelatin, or other glutinous substance, with an aniline or other dye-stuff. An ink in dry form protected by *Ashton* (Eng. Pat., No. 14,388, 1889) is prepared by drying a solution of a soluble colouring containing gum, etc., on wood shaving, gelatin, etc.; and similar patents were granted to *Nienstadt* and *Goldmark* in 1894 for the process of coating granules of non-porous material with a pigment and bind material (Nos. 3236 and 5078). The ink claimed by *Spencer* (Eng. Pat., No. 21,830, 1897) consists of an aniline dye-stuff mixed with sodium bicarbonate and a dry acid, the object of the latter being to cause effervescence and thus distribute the pigment through the water.

A solid ink containing a water-soluble aniline dye, with graphite or kaolin clay, and an agglutinant is claimed by *Olsen* (Eng. Pat., No. 152,465, 1920).

Stencil Inks.

Inks intended for use with stencil plates require to be fairly fluid, and to yield characters which dry rapidly, and are not easily effaced.

Blue Stencil Ink.—A mixture of 2 parts of shellac and 2 parts of borax is boiled with water (say 25 parts), and the solution mixed with a sufficient quantity of ultramarine to give the desired colour.

Black Stencil Inks.—(i.) The shellac and borax solution described above is mixed with a suitable proportion of lamp-black or nigrosine instead of ultramarine.

(ii.) A mixture of 2 parts of manganese sulphate with 1 part of lamp-black and 4 parts of sugar is ground to a paste with a small quantity of water, and a little gum arabic added to give consistency.

SHOW CARD INK.—An ink of similar character to the preceding

inks has been recommended for marking show cards and tickets for shop windows. It consists of 16 parts of asphaltum, 18 parts of Venice turpentine, 4 parts of lamp-black, and 40 parts of turpentine oil, thoroughly mixed together.

STENCIL DUPLICATION OF TYPEWRITING.—Inks intended for the duplication of typewriting by means of a wax stencil need special characteristics. Thus, they must flow readily from the roller, and not clog the stencil sheet, they must dry rapidly on the paper, and the pigment must not separate from the medium either on the roller or by " spreading " on the paper.

These qualities are obtained by the use of special pigments incorporated with a medium which is sufficiently volatile and of a suitable viscosity. Some of these inks contain only a soluble aniline pigment, whilst in others a carbon black in colloidal form is present.

The medium may consist of a mixture of an essential oil, with a suitable vegetable oil or hydrocarbon oil of the right viscosity.

The inks on the market vary considerably in composition, and the methods of making them are kept as trade secrets.

Machine Ruling Ink.

The inks in machines for ruling lines are of semi-solid consistency and usually contain ox-gall. A method of preparing the ink has been patented by *S.* and *R. Bezzant* (Eng. Pat., No. 8688, 1908). The raw ox-gall is heated to 220° F., 8 grms. of glycerin per pint added, the solution beaten with 8 grms. of gelatin at 212° F., and, after the addition of ink-powder, cooled to a jelly.

Inks for Rubber Stamps.

Many of the inks used with rubber stamps consist of an aniline dye-stuff in a suitable fluid medium.

Black Ink.—This can be prepared from aniline black $\frac{1}{2}$, alcohol 15, and glycerin 15 parts. It is poured upon the cushion of the stamp, and rubbed with a brush.

Blue Ink.—Soluble aniline blue, 3 ; distilled water, 10 ; acetic acid, 10 ; alcohol, 10 ; and glycerin, 70 parts. The blue is mixed with the water in a mortar, the glycerin then gradually added, and lastly the other ingredients.

Inks of other colours are prepared in the same way, other dye-stuffs being used in place of the blue. For example, methyl violet, 3 parts ; fuchsine, 2 parts ; methyl green, 4 parts ; nigrosine (blue-black), 4 parts, etc.

A bright red ink can be obtained by using eosine, but in this case the acetic acid must be omitted.

Reissig's Cancelling Ink.—An indelible ink intended for use with rubber stamps has been devised by *Reissig.* It consists of the following ingredients:—Linseed oil varnish, 16; fine lamp-black, 6; and ferric chloride, 2 to 5 parts. This ink must not be used with metal stamps.

Beyer (Ger. Pat., No. 224,637, 1910) claims the use of pigments obtained by the action of aldehydes, and especially formaldehyde, on ammonium ammonium oxyferrigallate or analogous compounds (see p. 88). The insoluble precipitates are washed, dried, and ground up with oil and glycerin or with aqueous solutions of shellac to form inks for stamping pads, waterproof drawing inks, etc. By the action of ketones, and especially acetone, colouring matters soluble in water and suitable for inking ribbons, stamp-pads, etc., are obtained (Ger. Pat., No. 229,467, 1910).

Inks for Typewriters.

The method of inking used in most typewriting machines is to draw a ribbon saturated with the ink between the type face and the paper, whereby, when a key is struck, the pressure conveys a certain amount of the pigment to the paper.

In some machines, however, the types are inked upon a pad before being brought into contact with the paper.

Whichever method be employed, the requirements of the ink are substantially the same. It must be sufficiently concentrated not to be rapidly exhausted in use, and it must remain permanently fluid when distributed through the ribbon or in the pad.

The earliest inks used for typewriters were strong solutions of aniline dye-stuffs in spirit or water, with an addition of glycerin to prevent the ink from drying too rapidly, and inks of this type are still on the market.

Methyl violet or methylene blue was frequently employed for the purpose, but other soluble dyes of sufficient intensity were also used. In the case of nigrosine care must be taken to have the powder perfectly distributed through the medium, since it does not dissolve like methyl violet. Hence, Induline blues, which are readily soluble, are sometimes used in the preparation of a very dark blue ink, which appears blue-black upon the paper.

In the preparation of the ink *Schweitzer* * recommends the fol-

* *The Distillation of Resins*, Chap. xvii. (Inks for Typewriting Machines), p. 176.

lowing method :—About 100 grms. of the dye are gently heated with a mixture in equal parts of glycerin and water (say, about 100 grms.) until completely dissolved. It is then cooled, and if any dye-stuff crystallises, more of the diluted glycerin is added and the mixture again heated. This process is continued until a cold saturated solution of the colouring matter is obtained.

If the ink, when distributed through the silk ribbon, gives impressions that are too faint, it contains too little glycerin. On the other hand, blurred or smudged impressions indicate the presence of too much glycerin.

Dirty, gritty impressions or irregular distribution of the pigment are due to the dye-stuff not having been completely dissolved.

Glycerin also causes the ribbons to absorb moisture from the air, and thus alters the composition of the ink. To remedy this fault hot oleic acid was used as the solvent, and the ink diluted to required consistence with a mineral oil.

As a rule typing inks are far less permanent than iron-gall inks, but there are some on the market which contain carbon pigments and will resist the action of any chemical agent.

Modern Typewriting Inks.—The tendency of the modern inks for typewriters is to approach more nearly to the type of printing inks—that is to say, insoluble pigments are used to a large extent.

The pigments require to be just as finely ground as in the case of printing inks, and the grinding is repeated several times in cylinder mills similar to those used for grinding painter's colours.

The black pigments used are lamp-black and carbon black, whilst the mineral pigments used include Prussian blue for blue inks and antimony cinnabar (made by heating antimony sulphide in a current of air and steam) for red inks, since vermilion is too expensive.

Lakes made as described (on p. 243) are also used as pigments, and special colours are prepared by blending pigments, as in the case of printing inks. If necessary, the tint of the ink is reduced by the addition of zinc white.

The uniformly ground pigment is first made into a smooth paste, with vaseline or a mixture of a heavy mineral oil and paraffin wax, and this paste is afterwards incorporated with about 10 per cent. of a fatty oil or oleic acid in which a suitable soluble pigment has been dissolved, and finally the mass is ground up in special mills until a product absolutely free from grit is obtained.

Walther * gives the following example of a black typing ink :—Ten parts of finely ground lamp-black are mixed with 40 parts of

* *Chem. Zeit.*, 1921, xxi., 169.

vaseline, and then incorporated with 5 parts of an approximately 50 per cent. solution of nigrosine in oleic acid, and the whole ground until of a uniform consistence.

In the case of coloured inks, the appropriate pigments are mixed together and blended with vaseline or mineral oil, after which the tint may have to be corrected by the addition of zinc white, this having been ascertained by means of practical tests. Finally, the mass is thoroughly ground as described.

Copying Typing Inks.—When copies of typewritten matter are required, it is necessary to use soluble pigments instead of the insoluble pigments. Basic dye-stuffs, such as methyl-violet, malachite green, safranine, etc., are frequently used for the purpose, and are ground up with vaseline, which is more suitable than mineral oil for the purpose. They yield dull impressions when typed, but give bright copies.

According to *Walther* (*loc. cit.*), castor oil or sesamé oil is used instead of vaseline in some factories. An ink of this type claimed in an old German patent (No. 71,912) has the following composition :—Twenty-four parts of the pigments are mixed with tar oil, and dissolved in a mixture of 4 parts of castor oil, 2 parts of creosote or phenol, and 2 parts of cassia oil.

In other inks the aniline dye-stuffs are dissolved in solutions of saponified oils.

Typewriter Ribbons.—The fabrics used for the manufacture of typewriter ribbons were formerly made of silk, but are now composed of a fine-meshed cotton woven for the purpose and in such a way that the edges are not displaced by the blows of the type.

Walther (*loc. cit.*) states that the old process of saturating the ribbons with ink, by passing them under rollers at each end of a vessel filled with the ink, is still used in certain works. Such ribbons give very clear impressions at first, but the ink becomes exhausted before the fabric is worn out.

For this reason, the principle used in the more modern processes is to attach a layer of the ink to each side of the ribbon. The apparatus used for the purpose comprises a series of rollers, through which the ribbons are made to pass in a continuous length. One of these rollers is coated with a film of the ink paste, which the pressure of the second roller causes to adhere to one side of the ribbon, after which the other side is similarly coated with the ink. Finally, the ribbon is mechanically cut into measured lengths, rolled, and packed in tin boxes with close-fitting lids.

CARBON PAPERS.—For taking copies of letters on a typewriter, one or more carbon papers are used. These consist of a tough

unsized paper coated on one side with typing ink. The inked side is placed over the paper to receive the copy, while the blank side is below the surface of the paper on which the original impression is to be made. The force of the blow then conveys pigment from the ribbon or pad to the top sheet, and also from the carbon paper to the second sheet. In this way it is possible to make several copies at a time, although when more than two are made there is some mechanical strain on the machine.

The nature of the pigments used for coating these papers varies with different manufacturers, and the particular formulæ employed are naturally kept secret. Apart from such details, however, the process of manufacture is much the same in most works, and the writer is indebted to *Mr. C. T. Smoothy* for many of the following particulars :—

Paper.—Different kinds of paper are needed for the manufacture of different sorts of carbons, and it is usual to select the quality in accordance with physical and chemical tests. For example, a paper composed of rag and wood pulp may be used for pencil carbons, but for pen carbons only rag paper is suitable. The paper intended for typewriter carbons must have a special texture, so that it will receive uniform blows from the type and yield its pigment without the application of force. Sometimes the paper has a selvedge, so that it can be gummed into a main folding book.

Compositions for Carbon Papers.—The black sheets still used in manifold books for taking copies of pencil writing are coated with a mixture of lamp-black, oil, and wax, and the composition is varied according to the use for which the paper is required.

In *Carter's* patent (Eng. Pat., No. 22,195, 1903) oil and glycerin are added to printing ink to form a backing for the stencil sheets of typewriting machines. In this way absorption of wax from the stencil sheets is prevented.

Lamp-black and carbon black are still used as black pigments in various modern carbon papers, and have given the general name of "carbons" to these products, which is retained even when coloured pigments are used.

Prussian blue is also a constituent of some of these compositions, frequently in association with lamp-black, but very careful grinding to insure a product free from grit. Organic lakes of red, blue, and green dye-stuffs, similar to those described on p. 243, are also used as pigments for these papers.

The chosen mixture of pigments is mixed with a suitable medium, which may include a large number of substances such as carnauba wax, montan wax, paraffin wax, ceresin, petroleum jelly (vaseline),

castor oil, oleic acid (oleine), bituminous pitch, stearic acid, etc., etc. The blend of waxes is chosen to raise the melting point to a sufficient degree to prevent the composition from smudging the typing paper too readily, and the more fluid constituents to prevent its adhering too firmly to the carbon paper.

It is obvious that an analysis of such paper compositions is a most difficult problem, although by treating the paper with successive solvents, such as hot dilute acetic acid, ether, petroleum spirit, alcohol, etc., it is possible to fractionate the constituents into groups, the physical and chemical characteristics of which will give some information as to their nature.

After thorough admixture of the pigments with the wax and oil medium the paste is ground between rollers of granite and steel until of uniform consistence, very much in the way in which printing inks are ground.

Coating the Paper.—The rolls of paper are 18 or 26 inches in width, and weigh from 70 to 80 lbs. They are made to pass over the rollers of the coating machine, which can be either heated with steam or chilled by an internal current of water, as required, rapid cooling of the coated surface of the paper being also promoted by a current of air from a fan or other device.

The ink is put into a trough, and is brought into contact with papers on the rollers as they revolve, the supply being regulated by means of devices termed "equalisers," whereby the quantity of ink applied to the paper is only just sufficient to solidify readily without leaving a sticky surface. The success of this operation depends upon the experience of the workman.

After receiving its layer of ink composition the roll of paper is re-wound upon a drum, and is subsequently cut into different sizes (demy, double crown, etc.).

The wave-like appearance of the surface of certain makes of pen carbon and typing carbon papers is produced by the vibrating action of a brush, known as the jigger, which is attached to the machine.

In the trade pencil carbon papers are known by the numbers, 7, 10, 15, 18, and 20, these indicating the weights in pounds of 500 sheets, each measuring 20 by 30 inches, whilst pen carbons are known as 5's, 7's, and 10's.

The terms "semi" or "full" are given to pencil carbons according to whether they are coated on one side only or on both sides.

WATERPROOF INKS.—This name is given to inks used by draughtsmen for drawing designs which will not be affected by water when dry. They consist of black or coloured pigments,

which are frequently aniline dye-stuffs, dissolved in a solution of a resin in alcohol or other suitable medium, which, on evaporation, leaves the resin and pigment attached to the surface of the paper, the resin protecting the dye-stuff from the solvent action of water.

Shellac is used as the resin for pale coloured inks, whilst ordinary rosin is suitable for darker pigments. In some of these inks the resin is dissolved in water in the form of an alkali boro-resinate.

Inks for Writing on Glass.

HYDROFLUORIC INKS.—One of the simplest fluids used for marking glass is a dilute solution of hydrofluoric acid, which reacts with the silica in the glass, forming a permanent etching.

The objections to the use of free hydrofluoric acid are that it is unpleasant to handle, and that it must be kept in a bottle composed of material—*e.g.*, gutta-percha—upon which it does not act.

It is far better to use a solution of a fluoride which is only mixed with an acid solution when required, as in the case of the following preparation :—

Solution I.—Sodium fluoride, 36 parts; potassium sulphate, 7 parts; distilled water, 500 parts.

Solution II.—Zinc chloride, 14 parts; hydrochloric acid, 65 parts; water, 500 parts.

Equal parts of the two solutions are mixed, and the writing done with a clean quill pen. The etching in the glass appears after about thirty minutes.

RESIN INKS.—An ink which gives writing not removed from glass by water is prepared by mixing together the following substances :—Turpentine, 15; shellac, 10; Venice turpentine, 3; and lamp-black, 3 parts.

Another formula for a fluid for writing on glass is as follows :—Resin, 20; alcohol, 150; borax, 35; methylene blue, 1; and water, 250 parts.

SILICATE INK.—An ink for writing on smooth surfaces such as metal or glass has been patented by *Rosenhain* (Eng. Pat., No. 26,951, 1903). It consists of a mixture of a strong solution of a silicate of potassium or sodium (soluble glass) with dilute sodium or potassium aluminate, and a suitable pigment, with or without the addition of sodium bicarbonate. This ink resists the action of mechanical abrasion and cold chemicals, but is removable by hot concentrated alkaline solutions.

FOERTSCH'S PENCIL FOR GLASS.—Eight parts of white wax are fused with 2 parts of tallow, and a pigment such as lamp-black or Prussian blue stirred in while the mixture cools. When nearly cold, it is rolled into pencil form on a slab, and covered with a paper case.

INKS FOR WRITING ON METALS.

Inks for Metals in General.—A black ink which can be used for writing on clean metallic surfaces is obtained by melting 5 parts of copal, then cautiously adding 6 parts of turpentine oil, little by little, and finally stirring 1 part of lamp-black into the mixture.

For a red ink $\frac{1}{2}$ part of cinnabar is used in place of the lamp-black, and inks of other colours can be prepared by the use of suitable proportions of pigments, such as Prussian blue, aniline dye-stuffs, etc.

These inks should be thinned with oil of turpentine to the required degree of consistence.

Ink for Zinc Labels.—An ink intended for writing on the zinc labels attached to plants was devised by *Puscher*.* It consists of 1 part of potassium chlorate and 1 part of copper sulphate, dissolved in 18 parts of water, and thickened with a little gum arabic. The writing is black, and will resist a fairly high temperature.

A blue ink for the same purpose is obtained by dissolving 60 parts of potassium chloride and 120 parts of copper sulphate in 1,400 parts of water, and mixing the solution with a solution containing 1 part of soluble aniline blue, and 100 parts of dilute acetic acid in 400 parts of water.

Black Ink for Iron, Zinc, or Brass.—A dull black writing is produced on these metals by an ink of the following composition:—Copper sulphate, 5; dilute (5 per cent.) acetic acid, 1; gum, 2; and lamp-black 1 part, mixed with 5 parts of water.

Ink for Copper or Tin.—For these metals the ink described in the preceding paragraph must be modified thus:—Copper sulphate, 5 parts; ammonium chloride, 3 parts; hydrochloric acid, 3 parts; gum, 2 parts; and lamp-black 1 part, in 5 parts of water.

Ink for Silver.—Yellowish-brown characters are produced on silver by a 7 per cent. solution of the double chloride of gold and sodium, and the colour is changed to black on exposure to the action of light. A solution of platinum chloride can also be employed as a black ink for writing on silver.

* *Wagner's Jahresber.*, 1873, xix., 206.

Inks for Writing on Leather.

The leather is first treated with a 10 per cent. solution of gallotannic acid, containing 1 per cent. of gum arabic, and then dried. It can then be written on with an iron ink of the following composition :—Ferrous sulphate, 2 ; gum, 3 ; and water 20 parts, to which a little indigo carmine is added to give a temporary colour, pending the formation of the iron gallotannate in the leather.

Ink for Ivory Surfaces.

*Lehner** recommends the use of solutions of silver nitrate ranging in strength from 10 to 1 per cent., according to the depth of tint required. The ivory is prepared by being immersed in a strong solution of ammonia, and washed with water. The writing may be toned to a brown colour by treatment with a 1 per cent. solution of sodium gold chloride, and fixed in a 10 per cent. solution of sodium thiosulphate (hypo).

An ink suitable for writing on ivory or waxed paper is claimed by *Ostwald* (Ger. Pat., No. 218,531, 1908). A small addition of a volatile organic compound soluble in water and containing not less than four atoms of carbon in its molecules is added to the ink. For example, up to 1 per cent. of valeric or caproic acid is added to an acid writing ink.

Ink for Writing on Wood.†

The surface of the wood is repeatedly brushed with a boiling solution of gelatin, and then sponged with a mordant containing 10 parts of alum, 2 parts of hydrochloric acid, and 10 parts of tin chloride in 50 parts of water. Writing of different colours may then be done on this prepared surface with solutions of various pigments, such as cochineal (red), decoction of Persian berries (yellow), decoction of anacardium seeds (black), potassium permanganate (brown), decoction of logwood (blue), etc.

Fireproof Inks.

Numerous inks have been described which, when used with a specially prepared paper, produce writing that resists the action of fire. Speaking generally, these contain some incombustible material, such as graphite or a metallic compound, which leaves a residue of oxide or metal when heated, and are used with a paper containing more or less asbestos fibre.

* *Die Tinten Fabrikation,* p. 228.

† *Die Tinten Fabrikation,* p. 228.

The use of such paper with a plumbago ink was claimed by *Halfpenny* in 1873 (Eng. Pat., No. 262), whilst *Hyatt* (Eng. Pat., No. 3684, 1873) also claimed the addition of asbestos to the raw material of paper.

In 1881 *Meihé* patented (Eng. Pat., No. 3410) fireproof inks for writing or printing on paper containing asbestos and wood fibre. These inks contained 5 or 10 per cent. of platinum chloride.

Meihé's Writing Ink.—Platinum chloride, 5; lavender oil, 15; Indian ink, 15; gum arabic, 1; and water, 64 parts.

Fireproof Graphite Ink.—Graphite, 85; copal varnish, 0·08; ferrous sulphate, 7·5; and tincture of galls 30 parts, with sufficient indigo carmine to give the required bluish colour.

Fireproof Paper.—Wood fibre, 1 part; asbestos, 2 parts; borax, 0·1 part; and alum, 0·2 part.

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LIST OF ENGLISH PATENTS.

WRITING AND COPYING INKS.

Date.	No.	Name.	Subject-matter.
1688	258	Holman.	Powder for black ink. To [illegible] mixed with water, beer, &c.
1764	809	Cummings.	Composition for writing [illegible] skins, paper, &c.
1768	906	Dring.	Making ink into a cake or solid.
1780	1244	Watt.	Copying presses and ink.
1809	3214	Fölsch and Howard.	Permanent writing ink.
1825	5285	Giroud.	Ink from chestnut wood ("damajavag").
1837	7313	Stevenson.	Indelible safety paper (impregnated with $MnCl_2$ and $K_4Fe(CN)_6$).
1837	7341	Aldrich.	Colours rendered applicable to writing.
1837	7342	Stephens and Nash.	Indelible ink. Carbon in solution of resinous soap.
1837	7474	Whitfield.	Indelible ink. Lamp-black in linseed oil, &c.
1839	8175	Normandy.	Writing inks.
1840	8770	Scott.	Indelible ink. Gas-black, indigo and Prussian blue in gall and logwood ink.
1843	9667	Roberts.	Composition of ink.
1844	10,329	Mackenzie.	Writing fluids.
1846	11,474	Reade.	Indelible ink. Soluble Prussian blue in gall ink. Also red ink, marking inks, and printing inks.
1855	970	Dépierre.	Ink from decoction of alder flowers and iron salt.
1855	1676	Wood.	Lake of alum and cochineal dissolved in ammonia solution.
1856	342	C. and G. Swann.	Writing and copying ink. Chrome logwood ink.
1857	1112	Underwood.	Copying paper. Writing with logwood decoction, and moistening with K_2CrO_4 solution before copying.

Date.	No.	Name.	Subject-matter.
1858	1132	Henry.	Copying ink. Addition of glycerin.
1858	1996	Winstone.	Copying ink. Addition of glycerin. (*Prov.*)
1859	861	Ballande.	Safety paper. Paper impregnated with metallic salt. Ink, a solution acting upon the salt.
1859	1744	Scoffern.	Ink. A solution of animal or vegetable fibre in "copperised" ammonia.
1860	388	Ballande.	Safety ink and paper. On lines of pat. of 1859.
1860	534	Melville.	Indelible ink. Plumbago with resin, gum, &c., alum, and a suitable colouring-matter.
1861	2972	Stevens (Croc.).	Indelible anti-corrosive ink. Aniline dyes used with carbon.
1862	675	Clark (Annaud).	Inks from aniline dyes.
1862	1213	Roberts.	Copying ink. Use of glycerin, molasses, and extract of *albemosch* seeds.
1862	2235	De la Rue.	Writing inks from aniline waste, &c.
1863	1418	Friederich.	Ink from logwood and potassium bichromate and ferrocyanide.
1863	1819	Goold.	Alkaline tannate or logwood solution treated with metallic iron. (*Prov.*)
1864	2223	Baildon.	Safety ink and paper. Colour of paper changed by acid in the ink.
1864	2506	Newton.	Method of oxidising ink. (*Prov.*)
1865	836	Newton.	Do. do. do.
1865	2267	Ellis.	Indelible inks. Colouring-matters precipitated by silicic acid and dissolved in a soluble silicate solution.
1867	106	Cooley.	Ink powders. Prepared by extracts of dye-stuffs with metallic salts, &c.
1868	2163	Cooke.	Copying ink. Addition of glycerin. (*Prov.*)
1869	47	Cooke.	Copying ink. As in the patent of 1868.
1870	1863	Pinkney.	Ink from aniline salts with oxidising agent and metallic salt, of which nickel is specially claimed.
1871	2745	Pinkney.	Ink from aniline salt, oxidising agent, and uranium or vanadium salt.
1873	258	Gutensohn.	Ink from tin waste.
1873	262	Halfpenny.	Incombustible ink and paper. Addition of asbestos to paper. Plumbago ink.
1873	1982	Carter.	Oxidising gall ink by air current.
1873	3814	Teysonnières.	Prevention of deposits in ink by addition of oxalic acid or oxalate.

Date.	No.	Name.	Subject-matter.
1873	3684	Hyatt.	Incombustible paper and ink. Addition of asbestos.
1874	1078	de Zuccato.	"Papyrographic" [copying] ink. Paper coated with varnish. Ink, a solution of caustic alkali with colouring matter.
1874	1839	Gaffard.	Indelible ink. Carbon in solution of alkali silicate.
1874	2009	Casthelaz.	Ink obtained by oxidising H_2SO_4 solution of aniline.
1874	2939	Mitscherlich.	Tannin for ink extracted by heating the substance containing it with sulphurous acid under pressure.
1874	3150	de Zuccato.	Improvements in Patent No. 1078 of 1874.
1874	4090	Petit.	Copying-ink pencil. Aniline dye with plumbago and adhesive material. (*Prov.*)
1874	4421	Knab.	Black for ink obtained by heating gas-tar with lime in a retort.
1875	1620	Grawitz.	Manufacture of aniline black.
1875	4484	Joly.	Ink prepared by action of tungstic acid on colouring matters (*e.g.*, of logwood, elderberry, &c.).
1876	974	Byford.	Dry copying ink powder.
1876	4820	Plateau.	Portable ink. Absorbent material saturated with aniline dye, &c.
1877	2389	Kromer.	Sympathetic ink. Dry tannin and anhydrous ferrous sulphate made into paste with benzene and varnish.
1878	1586	Jacobsohn.	Copying ink powder. Solution of aniline dye, sugar, gum, &c., evaporated to dryness.
1878	2636	Richmond.	Indelible ink, containing aniline black, and also the substance for forming aniline black.
1878	4606	Kwayser and Hasak.	Copying ink. Aniline colour in alcohol and water.
1878	5122	Hickisson.	Ink from vanadium or its salts with oxidising agent to form a mordant (pref. salt of nickel or copper).
1879	526	Fargue.	Ink attached to cavity of pen by adhesive material.
1879	2256	Rosefeld.	Copying apparatus (gelatin) and aniline ink.
1879	3391	Jefferies.	Aniline inks.
1879	3499	Taylor.	Formation of aniline black [also as marking ink]. (*Prov.*)
1879	4187	Hardt.	Aniline and metallic inks for copying apparatus.

Date.	No.	Name.	Subject-matter.
1880	2606	Bergel.	Marking fluid for paper silhouettes [KNO_3 solution]. (*Prov.*)
1881	741	Stoddart.	Manufacture of ink from spent tan liquors.
1881	963	Grünwald.	Dry copying ink. [Uranium acetate, sugar, glycerin with logwood extract and alum, or aniline colour]. (*Prov.*)
1881	1002	Priestman and Longshaw.	Ink from waste tan liquor and iron salts. (*Prov.*)
1881	2948	Schmitt.	Copying apparatus. Gelatin with glycerin and chrome alum. Ink which contains uranium salt and colour (*e.g.*, indigo), acts chemically on substance in the jelly.
1881	3410	Meihé.	Fireproof ink. Writing or printing with ink containing platinum chloride on paper containing asbestos.
1881	3605	Gurney.	Ink from spent tan liquor and iron filings.
1881	3657	Sachs.	Sensitive ink for tracing designs. Action of light on bichromate.
1882	728	Reissig.	Indelible ink. Printing ink incorporated with ferrous and ferric salts, and thinned with turpentine, &c. (*Prov.*)
1882	3083	Detmold	Aniline or gall inks, containing alcohol, spirit of camphor, &c. Drying instantly on contact with the paper.
1883	859	Fonseca & Co.	Indelible ink. Logwood extract, sugar, aniline black and soot.
1883	3600	Bolton.	Non-smearing copying ink. Addition of ginger and gum arabic to iron gall ink. (*Prov.*)
1884	7160	Friend.	Papyrographic ink. Iron, tannic acid and glycerin.
1885	440	Armour.	Ink removable by washing.
1885	8241	Frusher.	Ink from waste logwood, and potassium bichromate of dyeing vats.
1885	9249	Wass.	Indelible ink from carbonised sugar scum.
1886	3179	Payne.	Ink tablet for inking rubber stamps.
1887	730	Himly.	Sympathetic ink. Magnesium platinocyanide.
1887	15,079	Hackney.	Addition of $CaCl_2$ to ink to prevent drying. Blotting paper containing sodium sulphate or borate to decompose the $CaCl_2$, so that the writing can dry.
1887	17,925	Groth.	Indelible ink. Black compound from aniline in suitable medium.

Date.	No.	Name.	Subject-matter.
1888	648	Dimitry.	Solution of aniline colour with gelatin and potassium bichromate. Exposed to sun.
1888	7149	Smith.	Manifold copying ink (aniline in water, HCl and alcohol), used with slab of china clay, starch, glycerin, and water.
1888	7472	Quelch.	Invisible ink. Writing with solution of KNO_3 or KCl on non-glazed surface, and applying hot wire.
1889	2360	Brasier and Knowles.	Writing ink composed of alkaline extract of fibrous plant, *Bauhinia Vahlii.*
1889	8971	Mills.	Sanitary ink. Addition of an antiseptic agent.
1889	14,388	Ashton.	Dry inks. Soluble colours with gum, &c., dried on wood, shavings, &c.
1889	15,565	Pulford.	Invisible ink for envelopes. Uranium acetate and potassium ferrocyanide with white lead applied with lithographic varnish. Steam brings about reaction.
1890	2011	Conrad and Lilley.	Copying ink. Addition of indigo carmine and aniline black with glycerin and magnesium chloride to an iron gall ink.
1890	2130	Tschofen.	Invisible ink. Writing on smooth surface with chalk water and dusting letters with powder, *e.g.*, graphite.
1890	10,401	Conrad.	Copying ink. Addition of deliquescent salts (*e.g.*, ammonium nitrate), and glycerin.
1890	10,905	Piffard.	Copying paper. Paper treated with gallic acid—iron ink. No press required.
1890	15,857	Higgins.	Ink for stamps. Oleic acid and dyestuff, *e.g.*, methyl violet.
1890	15,858	Higgins.	Idem. Solution of aniline colour in essential oil.
1890	16,757	Just, Weiler, and Heidepriem.	Safety ink. Carbon black, vanadium compounds, galls, &c.
1890	17,373	Beales.	Copying ink and prepared paper. No damping paper required.
1891	1616	Leech and Harrobin.	Indelible ink. Turpentine, asphalt, resin, alum, beeswax and colour.
1891	3247	Coën.	Copying ink. Glycerin and candied sugar in ordinary ink.
1891	5437	Sherwood.	Copying ink. Soluble aniline dye, borax, water, and boiled linseed oil.

Date.	No.	Name.	Subject-matter.
1892	93	Higgins.	Stamping ink. Aniline colour with fixed oil and carbolic acid.
1892	18,721	Friswell and Leeds.	Copying ink. Lamp-black in solution of aniline dye evaporated, and residue mixed with lithographic varnish.
1893	7263	Blancan.	Indelible ink. Aluminium powder with protective varnish.
1893	16,830	Hollyer.	Sanitary ink. Addition of juice of lesser celandine.
1894	3236	Nienstaedt and Goldmark.	Dried ink. Granules of non-porous substance covered with dried ink.
1894	5078	Nienstaedt and Goldmark.	Dried ink. Glass or metal, &c., coated with pigment and binding material.
1895	6938	Thacker.	Safety paper. Coated with colour. Ink removes the colour of portion written on.
1896	3459	Adams.	Sympathetic ink. Dilute H_2SO_4 (1 : 17); writing made visible by heat.
1896	17,226	Temple.	Non-staining ink. Addition of saline compound, *e.g.* ordinary salt.
1897	21,830	Spencer.	Dried ink. Aniline dye with sodium bicarbonate and acid to produce effervescence and diffuse colour in water.
1897	21,991	Möller.	Invisible and indelible ink. Alum and white garlic juice—visible on heating.
1898	5294	Izambard.	Use of Röntgen rays in writing.
1898	24,644	Lichtentag.	Indelible ink. Carbon in soap and water or other medium.
1899	6727	Kretschmann.	Sympathetic ink. Paper treated with solution of cobalt chloride. Ink a solution of rock salt.
1899	8976	Bachem.	Sympathetic ink. Two substances, *e.g.* cobalt chloride and magnesium platino-cyanide, one becoming visible the other disappearing on heating.
1899	14,957	Power.	Rapidly-drying ink. Tincture hamamelis, tincture of iron, and gum arabic in spirits of wine. Red ink from rose petals.
1900	1290	Izambard.	Copying by means of Röntgen rays.
1900	7367	Kretschmann.	Sympathetic ink. Paper treated with non-hygroscopic cobalt salt. Writing with solution of salt and substance (*e.g.* vinegar) to produce hygroscopic salt.

Date.	No.	Name.	Subject-matter.
1900	3807	Brown.	Copying paper. Paper treated on one side with hardened gelatin, and on the other with deliquescent substance (*e.g.* $CaCl_2$), and solution of substance not affected by writing ink. No damping required.
1904	4447	Smith and Beswick.	Copying ink. Contains logwood, iron chloride galls, glycerin and rose-water.
1904	17,624	Leisel and Küpper.	Gold and silver writing inks. Powder suspended in medium containing volatile constituent. Paper subsequently heated.
1904	25,092	Flack.	Carbon (lamp-black) suspended in linseed oil, thinned with turpentine, &c., Prussian blue also used.
1904	29,245	Ojeda and Quesada.	Copying ink. Addition of glycerin and sugar syrup.
1905	23,109	Rieder.	Sympathetic ink. Silver chloride in varnish. Silver print bleached in bath of sodium chloride and copper salt.
1906	1732	Morris, Smith, and Bawtree.	Copying ink. Ferric chloride as hygroscopic medium.
1906	5183	Valentine and Smith.	Invisible ink. Sulphuric acid, developed by heat.
1906	12,872	Wyse.	Invisible ink. Chloride or other salt of cobalt.
1907	4379	Simpson.	Indelible waterproof ink. Resinous solution in ammonia and water, with lamp-black, dextrin, and nigrosine.
1908	9108	Garzino.	Sympathetic copying ink. Alkaline potassium ferrocyanide with magnesium carbonate, graphite, water, and gum. Developed with alum, iron, and potassium bisulphate.
1908	9579	Claessen.	Copying ink containing di- or polyglycerin.
1908	9663	Johnson.	Ink powder. Emulsion of carnauba wax and soap solution mixed with pigment and thickening agent and evaporated.
1908	19,588	Elam.	Copying ink. Aniline black, nigrosine, water, glucose, and glycerin, with alkali.
1910	24,136	Flachaire.	Sympathetic ink. Double iodide of mercury and silver.
1910	29,389	Rüter.	Quick-drying ink. Addition of alcohol.
1911	7318	Flachaire.	Double iodide of mercury and silver mixed with other substances.

WRITING INKS.

Date.	No.	Name.	Subject-matter.
1918	114,601	Akashi.	Solid ink, consisting of mixture of dye, with dextrin, insoluble gum, tragacanth, mucilage, thymol, and lactic acid kneaded to produce a paste.
1918	117,117	Shinozaki.	Indelible ink. Mixture of carbon in caustic alkali solution with caustic alkali solution of induline.
1919	130,319	Schmidt.	Safety ink. Water-soluble pigments, including iron ferrocyanide, oxalic acid, Epsom salts (to fix colour), and a water-soluble oil (Turkey-red oil) to penetrate the paper.
1920	141,631	Tsutsumi.	Solid ink. Composed of extracts of gall and logwood, sodium salicylate, gum arabic, and a water-soluble dye, to which is added potassium ferrous tartrate.
1920	146,676	Alison, from Kaisha.	Anti-corrosive agent, composed of crushed borax and dextrin. Prevents corrosion in ink containing tannin and sulphuric acid.
1920	149,373	Serafin.	Ink for drawing on lithographic stone. Ordinary ink plus glycerin.
1920	152,465	Olsen.	Solid ink. Containing water-soluble aniline dye, comminuted graphite or kaolin, and dextrin or other agglutinant.
1922	187,732	Plauson's (Parent Co.), Ltd.	Colloidal solutions from mineral substances, dispersed in gum arabic solution, water-soluble silicate solutions, etc.

MARKING INKS.

Date.	No.	Name.	Subject-matter.
1848	11,474	Reade.	Ammoniacal solution of silver tartrate. Addition of gold salts.
1856	738	Bufton.	Platinum salt (Pt_2Cl_6), added to the silver. (*Prov.*)
1858	2316	Dunn.	Marking ink pencils. Silver salts with black lead or other provisional colouring-matter.
1864	1828	Möller.	Red ink. Madder with cochineal, magenta or carmine. Alum as mordant. (*Prov.*)
1864	2511	Möller.	Madder extract with alkali salt in alcohol + gum and vermilion. Alum used previously as mordant.
1877	379	Schroll.	Marking ink pencil. Composition of clay, silver nitrate, or other soluble silver salt and plumbago.
1878	5122	Hickisson.	Vanadium salts, with oxidising salt as mordant. For solid pencil, gum, dextrin, clay, &c., added.
1879	3499	Taylor.	Formation of aniline black within the fabric.
1880	1771	Johnson.	Impregnating fibres with mixture containing ortho-nitro-phenyl-propiolic acid, reducing agent and alkali, and developing with heat.
1880	1838	Sachs.	Formation of dye-stuffs from polysulphides of heavy metals.
1881	466	Johnson.	Use of sulphides or sulpho-compounds of alkali metals as reducing agents in previous patent.
1882	5946	Langbeck.	Coloured marking inks. Salicylic acid, turpentine oil, spirits of wine, glycerin, and colouring matter (vermilion, &c.).
1883	751	Hickisson and Langbeck.	Colour mixed with solution of caoutchouc in carbon bisulphide.
1883	752	Hickisson and Langbeck.	Colour mixed with base of arsenic pentoxide, turpentine, and glycerin. Pencils from same mixture.
1884	9149	Hickisson.	Pencil with marking point ($AgNO_3$ with KNO_3) at one end and mordant (pyrogallol, wax and borax) at the other.
1884	15,961	Hickisson.	Mordant for pencil. Moistened and applied to linen.
1885	3980	Simpson.	Mordants rendering ordinary writing insoluble in water.

Date.	No.	Name.	Subject-matter.
1888	647	Domitry.	Soluble colour with gelatin and potassium bichromate, writing exposed to sunlight.
1893	5316	Hickisson.	Aniline dyes soluble in oil dissolved in *e.g.* castor oil, and solutions thinned with turpentine. For pencils, mixed with suitable base.
1905	17,793	Thorpe and Briggs & Co.	Indigo salt T (*o*-nitro-phenyl-methyl-lacto-ketone) or other body converted by alkali into insoluble pigment, in a suitable medium.

PRINTING INKS AND INKS FOR MISCELLANEOUS PURPOSES.

1772	1012	Rowley.	Ink for printing playing cards in colours.
1821	4601	Martin and Grafton.	Soot of burnt coal-tar as pigment.
1831	6182	Smith and Dolier.	Delible ink for copying books.
1835	6906	Bird.	Printing ink. Use of a mineral earth as pigment.
1853	483	Goodell.	Use of residue from purification of rosin oil.
1853	1900	Gwynne.	Powdered coal as pigment.
1853	1920	Newton.	Use of residue from distillation of rosin oil.
1853	2243	Maumené.	Carbonised lignite as pigment.
1854	1575	Archer.	Paper carbonised with sulphuric acid as pigment.
1854	2490	De la Rue.	Addition of glycerin.
1855	32	Livesay.	Ordinary typographic ink mixed with varnish, rosin, and Venice turpentine.
1855	320	Kuhlmann.	Addition of silicates to letterpress ink.
1855	1918	De la Rue.	Addition of manganese borate.
1856	400	Grant.	Addition of odoriferous essential oils.
1856	516	Brooman.	Pigment from bituminous shale and schists.
1856	2206	Underwood and Burt.	Copying printing ink. (Gall and ferrous sulphate.)
1857	1112	Underwood.	Copying printing ink. (Logwood extract.)
1857	1518	Matthews.	Green ink. Chromium oxide and varnish.

Date.	No.	Name.	Subject-matter.
1857	1744	Seropyan.	Ink for cheques.
1858	1187	Stuart.	Residue from distillation of bituminous substances as pigment.
1859	130	Viette.	Lithographic ink containing gutta-percha.
1859	348	Moss.	Ink for cheques.
1859	1282	Hadfield.	Apparatus for varnish manufacture.
1859	2081	Collins.	Transfer ink.
1859	2399	Palmer.	Aniline by-product as pigment.
1860	388	Ballande.	Safety printing ink.
1860	1445	Thierry.	Pigment prepared from carbonised schist.
1860	2640	Neal.	Grinding mills.
1862	767	Brooman.	Inks for printing on glass.
1862	2654	Prince.	Use of petroleum products in lithographic varnish.
1862	3074	Croc.	Telegraph ink. Aniline in dilute alcohol, thickened with gluten.
1863	1564	McLean.	Pigment from shale. (*Prov.*)
1863	3204	Hughes.	Ink for cheques. Compound of stannic acid and chromium oxide.
1864	2854	Rowley.	Use of pitchy substance from distillation of cotton oil.
1865	3325	Newton.	Oil substitute prepared from glue or gelatin.
1866	367	Holmes.	Animal pitch (bone oil pitch) as lamp-black substitute. (*Prov.*)
1866	1737	Holmes.	*Idem.*
1868	2578	P. and W. Hodge.	Pigments. Oxides of iron heated with carbonised peat.
1869	439	Binko.	Indigo printing ink.
1869	2890	Kirchner and Ebner.	Delible printing ink. Ferric hydroxide with tannin in a varnish.
1869	2946	May.	Non-oleaginous inks. Glycerin, gums, and pigment.
1869	2993	Kloen.	Water-colour inks. Pigments with glycerin, gums, sugar or other substances soluble in water.
1869	3543	Edwards.	Photo-mechanical ink. Extra greasy ink.
1870	967	Jackson.	Grinding mills.
1870	1419	Lawrence.	Ink containing glycerin, gum, sugar, and pigment.
1870	1863	Pinkney.	Use of aniline salts with nickel salts and an oxidising agent.
1870	2762	Lake (Toppan).	Use of petroleum products.
1871	689	Lake.	Copying ink. Use of pigment soluble in water and of soluble gums.
1871	2745	Pinkney.	Use of aniline salt with salts of vanadium and nickel.

Date.	No.	Name.	Subject-matter.
1871	3365	McCready.	Apparatus for blending colours.
1873	2133	Little.	Telegraphic apparatus. Ink of aniline blue in glycerin.
1873	3129	Mackay.	Use of oil recovered from waste fabrics.
1873	3176	Newton.	Pigment for printing fabrics.
1873	3598	Kingdon.	Grinding mills.
1873	3684	Hyatt.	Fireproof ink. Addition of asbestos powder.
1873	3809	Smith and Fountain.	Heating printing ink to uniform temperature before use.
1873	4196	Thomas.	Use of heavy oils and pitches from tar.
1874	208	Clark.	Apparatus for manufacture of lamp-black.
1874	1078	de Zuccato.	Papyrographic ink. Caustic alkali solution and vandyke brown.
1874	1839	Tongue.	Carbon in a silicate solution as indelible ink.
1874	1995	Clark.	Stamping ink. Solution of colour in alcohol and glycerin.
1874	4421	Knab.	Manufacture of pigment from gas tar, &c.
1875	605	Whitburn.	Ink for printing on wood.
1875	1620	Clark.	Production of aniline black for printing.
1875	1941	Holyoake.	Transfer ink. (*Prov.*)
1875	3762	Edison.	Ink for autographic printing. Printers' ink thinned with castor oil.
1876	1662	Heuer.	Printing on glass.
1876	2268	Brooks.	Coloured printing inks. Special varnish.
1876	2621	Zingler.	Metallic printing inks. Solution of albumen as vehicle.
1876	3270	Tongue.	Pigments from anthracite and other coal. (*Prov.*)
1876	4470	Pinkney.	Ink for cheques. Use of ferrocyanides with aniline or vegetable colours.
1877	169	Tongue.	Pigments from anthracite, &c. (*Prov.*)
1877	895	Pumphrey.	Autographic ink. Aniline colours in acetic acid and glycerin.
1877	950	Williams.	Boiling oil. Use of steam.
1877	3402	Howard.	Pigment from peat charcoal.
1877	3407	L'Heureux and Ligny.	Engraving ink containing sugar, gum arabic, and silicates.
1878	2706	Liston.	Ink for printing on earthenware. Pigment with glycerin or molasses.
1878	5098	Winterhoff.	Ink for china, wood, iron, &c. Pigment with varnish of oil, resins, Venice turpentine, wax, suet and flux.

Date.	No.	Name.	Subject-matter.
1879	141	Haddan.	Metallic powder incorporated with solution of silicate.
1879	402	Cunnack and Argall.	Kaolin clay as a base for the pigment.
1879	2518	Gray.	Preparation of varnish by treating oil with hot air.
1879	3391	Jefferies.	Transfer ink. Treacle and glue.
1879	4204	Nesbit.	Ink for cheques. Aniline printing ink.
1879	4524	Gestener.	Water colour transfer ink. Mixture of a water-colour pigment in aniline with glycerin, varnish, syrup and mineral pigment. (*Prov.*)
1879	4645	Kesseler.	Ink for zincography. Pitch, tar oil, fatty acid, aniline violet and residue from distillation of rosin oil.
1879	4788	Imray.	Transfer printing inks.
1879	4997	Haddan.	Ink for cheques. Bichromate, ferrous sulphate, ferrocyanides, logwood, oxalic acid and glycerin. (*Prov.*)
1879	5232	Wirth.	Coal tar as pigment. (*Prov.*)
1880	827	Pfleiderer.	Ink for glass. Pigments with copaiba balsam, Venice turpentine, rosin oil and driers.
1880	1028	Klein.	Ink for printing oil cloth.
1880	1615	Alexander.	Pigment from bitumens and hydrocarbons. (*Prov.*)
1880	1838	Sachs.	Use of dyeing substance in printing ink.
1880	1971	Savigny and Collineau.	Use of a special vegetable colouring matter.
1880	2216	Kesseler.	Ink from pitch, fatty acid, aniline violet, and tar oil.
1880	3418	Ungerer.	Colouring composition for impression rollers. (*Prov.*)
1880	4591	Bertram.	Flexible ink. Aniline, acetic acid, glucose, glue, glycerin and water.
1880	4693	Bastand.	Use of oil from cotton waste.
1880	4846	Witt.	Ink for calico printing.
1880	4874	Boult.	Ink for celluloid. Aniline colours in carbolic acid.
1881	375	Dupré and Hehner.	Ink for cheques.
1881	436	Poirson.	Transfer ink for leather, &c. Containing salts melting in their water of crystallisation, *e.g.* alum or sodium sulphate.
1881	814	Marie and Bouneville.	Use of nitric esters of sugars. (*Prov.*)
1881	903	Gard and Cobley.	Use of tannin black from leather waste as lamp-black substitute.

Date.	No.	Name.	Subject-matter.
1881	1002	Longshaw and Priestman.	Tannin black from spent tan liquors. (*Prov.*)
1881	1203	Brackebusch.	Printer's varnish without linseed oil. Colophony and paraffin oil. (*Prov.*)
1881	2103	Bastand.	Use of oil extracted from engine cotton waste.
1881	2274	W. G. and R. R. White.	Polychromatic printing ink containing aniline dye-stuffs, &c.
1881	2868	Jensen.	Ink from pitch, anthracene oil, tar oil, aniline colour and lubricating soap. (*Void.*)
1881	3410	Meihé.	Fireproof printing ink. Use of asbestos powder.
1881	3605	Gurney.	Tannin black from waste tan liquors.
1881	3657	Sachs.	Ink for impressions of patterns. Chromium compound, &c.
1881	3762	Clark.	Autographic transfer ink. Contains proteids, bichromates, ferrocyanides and alums.
1882	728	Reissig.	Indelible printing ink. Linseed oil varnish, lamp-black, and ferric chloride. (*Prov.*)
1882	3086	Wirth.	Manganese peroxide as pigment.
1882	3248	Gibson.	Metallic inks. Metallic powder mixed with naphtha and solution of rubber in carbon bisulphide.
1882	4106	Claus.	Iron sulphide incorporated with rosin, gum, or fused sulphur.
1883	949	Nesbit.	Ink for cheques. Use of decoction of alkanet root.
1883	3638	Lake.	Ink for india-rubber goods. Caoutchouc, naphtha, red lead, and sulphur.
1884	2268	Baseley.	Grinding mills.
1885	9249	Wass.	Pigment from sugar scum.
1885	9413	Macrone.	Varnish from seed oil, rosin, paraffin wax, beeswax, and copal varnish.
1886	606	Rousset.	Varnish for fixing transfers. Mineral pitch, heavy benzine, and copaiba essence.
1886	1601	Gutheil.	Lithographic ink of intense colour. Venetian soap, wax, mastic, shellac, Venice turpentine, lamp-black or soot rubbed with water for use.
1887	1076	Schlumberger.	Addition of vegetable colouring-matter (alizarine) altering colour on addition of alkali. (*Opposed and not granted.*)
1887	17,925	Groth.	Antiseptic ink. Aniline black in aniline, carbolic acid, &c.

Date.	No.	Name.	Subject-matter.
1888	3321	Bensinger.	Ink for celluloid. Aniline dye-stuff in carbolic or acetic acids.
1888	13,968	Neilson, Harrap and Brown.	Antiseptic ink. Use of permanganate or pigments used in sanitary wall-paper.
1888	15,457	Jones.	Invisible printing ink. Cobalt salt in dilute alcohol. Inking rollers to be covered with absorbent material, *e.g.* flannel.
1889	6287	Weight.	Sanitary ink. Part of paper rendered transparent with "medicating oil."
1889	8971	Mills.	Sanitary ink. Addition of antiseptic.
1889	15,839	Browne.	Use of semi-fluid bitumen (maltha) with or without black pigment.
1889	20,830	Huelser.	Use of fine coal dust as pigment.
1890	11,168	Holt.	Ink from residue from distillation of petroleum with resin, gum, and pigment.
1890	15,743	Davison.	Imitation metallic printing inks. Nitrobenzene aniline product, picric acid, varnish, spirit, soap, rosin, &c.
1890	16,689	Lake.	Non-clogging ink. Vaseline, fatty oil, and pigment.
1890	16,757	Just, Weiler, and Heidepriem.	Ink for cheques, &c. Black from sugar, or carbon black, caustic potash, oxalic acid, Indian ink, vanadium compound, galls, gum arabic, aniline colour, and water.
1891	873	Hudson and Hills.	Antiseptic ink. Permanganate or eucalyptus, &c., with glutinous compound.
1891	12,104	Brandt.	Zincographic ink. Antimony black, bone black, resins, strong varnish, Berlin blue and ordinary printing ink.
1891	12,200	Bertling.	Lithographic transfer ink.
1891	17,635	Dreyfus.	Resinates of coal tar dye-stuffs used as pigments.
1892	12,280	Chamberlain.	Ink for cartridge case. Varnish, pigment, and drying oil.
1893	7263	Blancan.	Metallic ink. Aluminium powder with protective varnish.
1893	12,863	Bibby.	Use of cotton seed "foots" with other usual ingredients.
1894	6268	Degroote and Aulnois.	Colour printing ink. Pigment, boiled linseed oil, siccative and caoutchouc.
1894	13,676	Cardeaux.	Printing from raised type on tin foil. Addition of vaseline to ink.

Date.	No.	Name.	Subject-matter.
1894	20,423	Barnwell.	Printing several colours in one impression. Inks in strips on rollers prevented from mixing by addition of castor oil, turpentine, tar oil, copaiba balsam, sulphuric ether, ammonia, and ipecacuanha.
1895	955	Priestley and Swann.	Metallic inks. Bronze powder, &c., with varnish and lard or fat.
1895	6938	Thacker.	Inks for wood, canvas, paper, &c. Surface covered with coloured layer which can be removed by suitable chemicals. (Cheque ink.)
1895	17,868	Hallet.	Printing ink for imitation typewriting. Aniline dye-stuff used.
1896	8376	Taylor and Cooke.	Printing in several colours in one impression. Inks prevented from mixing by addition of copaiba balsam, glycerin, sandal wood oil, petroleum, turpentine, tincture of myrrh, chloroform, and ammonia.
1896	12,198	Torrance.	Grinding and mixing mill. Differential gearing for rotating rollers at different speeds.
1896	16,274	Sharp.	Metallic ink suitable for stencil machines. Metallic powder with gum arabic, linseed oil, rosin oil, dextrin, red lead, litharge and turpentine.
1896	18,131	Michel-Dansac and Chassagne.	Coloured ink. Albumen preparations with specified coloured pigments.
1896	26,992	Webb.	Safety ink for copper and steel plate printing. Aniline colour in base of flour and magnesium oxide with sodium carbonate and soap.
1896	30,121	Boult.	Metallic ink (" *direct-or* "). Varnish and oils, rosin, &c., with bronze powder.
1897	7399	Gentele.	Cellulose or wood powder as substratum for colour.
1897	9121	Taylor.	Printing in several colours simultaneously. Addition of powdered manganese and alcohol to substances enumerated in Pat. 8376 of 1896.
1897	18,533	Ogilvy.	Mixed pigments and varnish incorporated by use of superheated steam or steam under pressure, and volatile products condensed.
1897	19,783	Webb.	Fugitive safety ink. Base of dextrin and treacle with glycerin, aniline dye-stuff and antiseptic agent.

Date.	No.	Name.	Subject-matter.
1897	23,080	Hadley and Sephton.	Ink for etched designs on glass, &c. Contains wax, Canada balsam, soap, and lamp black.
1897	24,504	Stoop.	Substitute for linseed oil. Use of drying mineral oils, *e.g.* grisee oil.
1897	29,728	Banner.	Substitute for linseed oil. Colophony in suitable solvent wholly or partially saponified with caustic soda or sodium silicate ; or use of lime-rosin.
1897	30,104	Burger.	Inks used in production of colour prints.
1898	5294	Izambard.	Radiographic or X-ray proof ink. Metallic or calcareous powder with boiled oil and alkali bromide.
1898	11,951	Gotliffe.	Printing waterproof fabrics. Metallic powder (nickel) with egg albumen or other thickening agent.
1898	20,356	Pitt.	Use of gelatinous compound from kelp.
1898	23,071	Stoop.	Use of natural drying mineral oil (grisel oil) in varnish.
1899	17,557	Printing Arts Co. and Orloff.	Use of inks of different consistency in colour printing.
1900	13,145	White.	Polychromatic printing. Special sheets of composition containing the colours.
1900	14,886	Ogilvy.	Admixture of ink effected by heating and mechanical agitation. No mill used.
1900	17,126	Hofer.	Ink for printing transparencies on celluloid. Pigments and mixture of ether, camphor, paraffin oil and manganese.
1900	17,783	Stevenson.	Printing designs changing colour on exposure. Use of combination of permanent and non-permanent colours.
1900	23,231	British Oil Mills Co. and Wass.	Use of residuum from purification of cotton-seed oil.
1901	1366	Hoz.	Use of dyeing pigments and development and fixing of printing on the fabric.
1901	5168	Imray.	Use of iodophenolthiosulphonates as pigments.
1901	6061	Wass.	Use of solution of rosin in mineral oil as varnish.
1901	8645	Tellkamp.	Autographic ink.

Date.	No.	Name.	Subject-matter.
1901	12,826	Wechsler.	Lithographic printing. Ink for continuous working. Pigment, varnish, glycerin, alkali salt, tartar, and turpentine.
1901	23,892	Lilienfeld.	Fixing varnish for pigments for textile fabrics.
1902	8371	Schmiedel.	Production of dark shade on coloured ground. Use of a solution of a resin with or without glycerin.
1903	3033	Ninnis.	Transparent letters on ground glass. Ink of Canada balsam, gum, &c., in turpentine or spirits.
1903	3301	Grabau.	Ink for washable wall-papers. Paste of potato-flour and borax with aniline dye.
1903	11,028	Préaubert and Thube	Casein made soluble with alkali as thickener for printing ink.
1903	12,681	Johnson, for Badische Co.	Compounds of colouring matter bases with fatty acids or their alkali salts used as printing inks.
1903	14,299	Braun.	Conducting ink for autographic *or* facsimile telegraphy. Use of acid solution of platinum, copper, &c., mixed with graphite.
1903	22,195	Carter.	Ink for backing sheet of typewriters. Addition of oil and glycerin to printing ink.
1903	26,951	Rosenhain.	Non-corrosive ink for glass, metal, &c. A mixture of alkali silicate solution with sodium or potassium aluminate and a suitable pigment.
1904	3909	Rowan.	Safety ink for cheques. Paper impregnated with ferrocyanide. Ink of ferric chloride, potassium iodide, and caustic soda.
1904	21,062	Bennett and Mastin.	Coloured glass, porcelain, &c., finely powdered and used as pigment.
1904	7931	Millar.	Coloured lithographic ink. Mixture of linseed oil and wax (6 : 1).
1904	24,733	Bennett and Mastin.	Potter's clay, mixed with pigment (*e.g.* cobalt oxide) and fired. Used for printing ink.
1904	25,202	Janzer.	Rapid-drying ink. Addition of 5 to 30 per cent. of mixture of pyroxyline, Canada turpentine, castor oil, alcohol and ether, in specified proportions.
1905	9809	Spencer and Lyst.	Solution of rubber and dye-stuff for printing calico or fabrics.
1905	11,049	Lamb and Rennie.	Ink for printing on leather.

Date.	No.	Name.	Subject-matter.
1905	12,128	Hart.	Polychromatic printing. Dye dissolved in solvent, mixed with vehicle (Fuller's earth), solvent evaporated, and residue ground with varnish.
1905	14,023	Lerck.	Ink for colour printing to prevent colours mixing. Balsam, glycerin, myrrh, petroleum, turpentine, alcohol, and manganese oxide added.
1905	14,464	Liscke.	Ink for printers' overlay sheets.
1905	19,328	Longley.	Basic dye-stuff in solvent (acetic acid) with phenol and gelatinous matter from carrageen or seaweeds.
1905	25,859	Fireman.	Ferroso-ferric oxide obtained by oxidation of ferrous hydroxide, used as pigment for printing ink.
1906	5050	Boult.	Ink for prepared wood. Chinese ink, gum arabic, and dilute acetic acid.
1906	9796	Bousfield	Printing ink for music. No varnish present.
1906	18,562	Imray.	Gelatin colours for printing from intaglio oiled formes.
1907	2998	Lilienfeld.	Silk-like effects. Ink contains a compound of zinc or other metal with viscose.
1907	27,312	Acheson.	Printing ink containing deflocculated amorphous material (graphite) with linseed oil, varnish, &c.
1908	8688	Bezzant.	Treatment of ox-gall for machine rulers' ink.
1918	27,233	Mansell.	Sensitizing ink for stencilled designs. Silver nitrate, water, alcohol, and glycerin.
1909	2144	Walker and Sohn.	Oil residues treated with sulphuric acid to make compound for printing ink.
1909	4040	Jagenburg.	Pigment for printing inks, obtained by mixing dyestuff with thickening material, and precipitating with barium chloride.
1909	16,291	Hochstetter.	Mimeograph ink. Pigment ground with Turkey-red oil.
1909	16,636	Lamp'l.	Bank notes printed in colours as permeable as the paper to actinic rays. Proof against photography (*e.g.* rhodamine, chrome alum solution, and alcohol).
1909	27,268	Escardó and Sala.	Cheque ink. Invisible impressions made visible by rubbing with a coin. Ink of zinc white and colourless varnish.

Date.	No.	Name.	Subject-matter.
1909	29,379	Sureties.	Brewers' yeast mixed with ground spent hops, dried, and used for printing ink.
1909	29,460	Newton.	Transfer ink for wood, glass, &c. Solution of soap with colour and barium sulphate.
1910	7722	Child.	Tar with shale or anthracite in printing ink.
1910	17,886	Laza.	Ink for printing on bread. Pigment with gum solution or dextrin, &c.
1910	19,156	Lorenz.	Cheque ink. Contains ingredient sensitive to reagents, such as the dye *Cotton* 4*B*, or dyestuff precipitated by tannin, &c.
1910	22,237	Simpson.	Cheque ink. Mixture of aniline dye with glycerin and printing ink.
1910	29,735	Pickstone.	Rubber stamp ink. Aniline dye with dextrin and glycerin.
1911	14,142	Lilienfeld.	Printing ink. Poly-fatty acid with cellulose or derivatives, pigment, &c.
1911	17,772	Hurwitz.	Hectographic ink.
1911	18,965	Lucas.	Transfer ink for photographic purposes.
1912	914	Wass.	Printing ink. Mineral oil with driers, pigment, &c.
1912	14,578	O. and C. Lauthe.	Transfer ink. Lithographic ink with asphaltum, rosin, fat, &c.
1912	16,570	Thomson.	Ink for coating carbon papers. Hydrocarbon oil, linseed oil varnish, Berlin blue varnish, Milori blue and indigo.
1913	5737	Turkin.	Printing ink from product of treating pigments with Turkey-red oil and alkali.
1913	6387	Lilienfeld.	Printing ink containing cellulose esters.
1913	10,035	Heyl and Baker.	Quick-drying printing ink. Contains amyl sulphate.
1913	12,567	Schütze and Fischer.	Dyestuff with albuminous vehicle or sulphonated oil.
1913	14,245	Sureties.	Peat fibre in printing ink.
1914	547	Quick.	Ink from residues from soap lyes.
1914	3370	Lilienfeld.	Use of carbohydrate esters in ink.
1914	4419	Wolff.	Printing ink. Fine mineral matter such as infusorial earth used.
1914	5011	Meister Lucius and Brüning.	Use of reduction dyestuffs as pigments.
1914	23,128	Turkin.	Improvements on Pat. 5737 of 1913.

Date.	No.	Name.	Subject-matter.
1915	118	Bray.	Turpentine as carrier of ink—to prevent stretching of paper.
1915	5,363	Travers.	Aniline ink, containing gum dissolved in rectified petroleum or naphtha, for slides for optical projection lanterns.
1915	7,284	Bakelite Ges. M.B.H.	Ink for printing fabrics. Dye-stuffs with water-soluble phenol and formaldehyde condensation products.
1915	10,089	Lipsius.	Ink for printing in imitation of embossed work. Slow-drying ink, followed by application of shellac, which is fused in place.
1917	104,429	Stevenson and Roneo, Ltd.	Printing and stencil duplicating ink. Calcium chloride in conjunction with gum, lamp-black and (or) aniline dyes.
1917	109,270	Sieger.	Utilisation of raw acid resins separated in the treatment of hydrocarbons with sulphuric acid.
1917	111,279	Soc. Anon. La Photogravure Rotative.	Printing, lithographic, and transfer ink. Use of resinous and gummy substances (other than camphor, india-rubber, and gutta-percha).
1918	116,109	C. Jäger Ges. and R. Waldemar Carl.	Ink composed of aniline suspended in water (with glue, gelatin, etc.) and a substance yielding formaldehyde when heated (*e.g.*, hexamethylene-tetramine), and so fixing the glue.
1918	117,023	Hope.	Ink leaving paper white when re-pulped. Sulphur dyes rendered soluble by sodium sulphide, precipitated as lakes, and mixed with oils, resins, or varnishes.
1919	131,769	Duke.	Starch, dextrin, etc., mixed with tannic acid and iron chloride to produce insoluble black pigment.
1919	134,959	Dixon.	Ink for match boxes. Printing ink, with active constituent (phosphorus, etc.) incorporated with any suitable printing composition.
1919	135,160	Lane.	Ink for producing legends in black on motion-picture negatives. Cotton-seed oil (5 parts) and citronella oil (1 part) added to printing ink to obtain more uniform distribution.
1920	148,650	Nelson.	Ink for printing coat label fabrics, etc. Lithographic ink mixed with paste dryer of the terebene and gold size type.
1920	149,319	Lilienfeld.	Use of alkyl or aralkyl derivatives of carbohydrates, $n\ (C_6H_{10}O_5)$, such as starch or dextrin, in printing compositions.

Date.	No.	Name.	Subject-matter.
1921	156,212	Chem. Fabr. Worms Akt.-Ges.	Aqueous lactate solution used for keeping colours moist in printing inks.
1921	159,809	Fitzgerald.	Dry lithographic ink composed of ordinary ink incorporated with grease-resisting and deliquescent materials.
1921	161,700	Hinley.	Inks for transferring patterns to knitted goods. Transfer printed with ink of pigments, lithographic varnish, tallow, stearine, and paraffin wax.
1921	166,117	Rütgers-werke Akt.-Ges.	Black printing ink containing resinous bituminous products from coal, etc.
1921	169,917	Parry.	Preparation of ox-gall free from sliminess, for ruling inks.
1921	171,661	Lilienfeld.	Use of esters of carbohydrates. Modifications of Eng. Pat. 149,319.
1921	172,588	Schiffmann.	Stamping ink. Aniline black (soluble in alcohol), with iron gallotannate, in acetin, with addition of carbon black.
1922	176,599	Aurich.	Inks for lithography.
1922	177,515	Mouberg.	Ink for multiplying cliches. Printing ink with wax, glycerin, and Indian ink.
1922	183,513	de Waele.	Printing and stencilling inks. Composed of mutually insoluble substances in the form of an emulsion.
1922	184,880	Plauson's (Parent Co.), Ltd.	Preparation of colloidal clay, especially China clay, in the colloid mill, for use in printing inks, etc.
1922	187,537	Smidt and Jaeger.	Printing ink from waste sulphite cellulose lyes by treatment with nitric acid and a catalyst (zinc or copper).
1922	190,203	Johnson.	Use of products recovered from coal gas.
1923	194,156	Ishida.	Non-smearing printing ink. Soluble silicate, tannin, insoluble soap, gum arabic, formaldehyde, and water added to printing ink.

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INKS

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MANUFACTURE

Jason Allen 4-27-05